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STRUCTURAL BIREFRINGENCE IN AMORPHOUS SOLIDS

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Received April 18, 1950

1. Introduction

The birefringence exhibited by optically isotropic solids when deformed by stress is familiar knowledge and forms the theme of the subject of photo-elasticity. There exists, however, a second kind of birefringence which may also be exhibited by amorphous solids and which differs both in its origins and in its observable characters from the photo-elastic effect. To distinguish it from the latter phenomenon, it has been designated as structural birefringence (Raman, 1950). The name is intended to convey the idea that such birefringence owes its origin to anisotropy of structure existing even when the material is free from stress. Such anisotropy is, of course, not a normal property of the material as in the case of crystals, but is "accidental" in the sense that it is a consequence of special circumstances existing during the formation of the solid. The recognition of such birefringence as a distinct phenomenon is compelled by a study of the facts observed with vitreous silica and described in the paper cited. Structural birefringence in the case of this substance manifests itself as streaks or sheets of luminosity—inexplicable on the basis of photo-elastic theory—which are clearly the result of flow in the material while in a plastic state before its final solidification.

The present paper describes similar studies made with other materials and especially with the inorganic glasses. The results show unequivocally that structural birefringence is also exhibited by such glasses, either by itself or in conjunction with the photo-elastic effect. As is well known, the process known as "annealing" is an essential part of the technique of glass manufacture. Its purpose is to remove the internal stresses set up in the fabricated material by differential rates of cooling of its parts, and the test applied to determine whether this has been accomplished is the disappearance of birefringence. Except, however, in the case of high-grade optical glass where special techniques are employed to obtain a perfectly homogeneous and isotropic product, the process of annealing never actually succeeds

in removing all observable birefringence. Indeed, the commoner commercial varieties of glass exhibit, when critically examined, an easily noticeable birefringence. It is with this phenomenon that we are concerned in the present paper.

As already noted in the paper on vitreous silica, the detection and study of a feeble birefringence needs the use of a light source of adequate intensity. The most satisfactory method is to place the object under examination between two crossed polaroid sheets, and send a beam of sunlight through it. For observation or photography of a large area of the object at one time, it will be necessary to diffuse the incident light beam by a sheet of ground glass. As polaroid sheets are available up to twelve inches square in area, quite large objects can be examined in this way. It is necessary that the surfaces of the object through which the light enters and emerges are flat and parallel. This requirement may be avoided by immersing the object in a flat-sided cell containing a liquid of suitable refractive index. But this naturally restricts the size of the objects which can be examined.

2. The Birefringence of Plate Glass

Common glass is produced commercially on a large scale in the form of sheets or plates of any desired thickness. The process of the manufacture and the annealing of the product are both so highly perfected that a sheet of quarter-inch plate glass when held normally between crossed polaroids usually shows no noticeable restoration of light. One might be tempted to infer from such an observation that the material is optically isotropic. Actually however, this is not the case, as becomes apparent when the plate is set and viewed edgewise between crossed polaroids, the light traversing the material in a direction parallel to its surfaces. A strong restoration of light is then noticed; this is a maximum when the plate is inclined at an angle of 45° to the principal planes of the polariser and analyser but, as is to be expected, vanishes when the plate is set parallel to either of these planes. The origin of the birefringence becomes evident when the edge of the plate is viewed through a magnifying lens in the circumstances stated. It is then seen that the entire thickness is made up of a great many laminæ parallel to the surfaces of the plate overlying each other (see Plate XIII). To see the laminæ clearly, it is necessary that they should be viewed in a direction accurately parallel to the surfaces of the plate; further, as already remarked, the edges through which the light enters and emerges should be flat and parallel. (Alternatively, the observations may be made with the plate immersed in a flat-sided cell containing xylene). The fact that the individual laminæ are birefringent and in varying degrees is evident

from the varying intensity of the restoration of light that they produce. The same may also be very elegantly exhibited by superimposing a quartz wedge on the edge of the plate; the straight fringes due to the wedge run at right angles to the plate and appear above and below it, while the fringes due to the combination of the wedge and the plate appear in the central strip. The course of the latter fringes then displays the birefringence of the individual laminæ very clearly (see Plate XIII).

The foregoing descriptions refer to the phenomena exhibited by a strip of plate glass at a sufficient distance from its free edges. At and near these free edges, however, we observe a restoration of light which is a distinct phenomenon, as is shown by its being most conspicuous when the strip is held in such a position (parallel to the principal plane of either the polariser or the analyser) in which the structural birefringence vanishes; it is evidently a photo-elastic birefringence produced by the stresses set up in the vicinity of the edges of the strip when it is cut. If the strip be inclined so as to restore the visibility of the structural birefringence, we notice a superposition of the two effects in the vicinity of the edges. Such superposition and the special features arising from it are particularly conspicuous when the plate under observation is thick, and its length is also not much greater than its thickness. A characteristic effect noticed is that a lamina which appears as a bright streak on one side of the plate changes over to a dark streak on the other side as it crosses a dark band of the photo-elastic pattern, and *vice versa*. Several examples of this effect are to be seen in the figures reproduced in Plate XIV.

It should be mentioned here that if the edges of a thick plate of glass are smoothed and polished, its laminated structure may be observed even without the aid of polarised light, by merely viewing the plate in a direction accurately parallel to its surfaces. The individual laminæ are then clearly visible, but they disappear if the plate be slightly tilted. If a narrow illuminated slit is observed through the edge of the plate, the laminated structure gives rise to various interesting optical effects ascribable to reflection and diffraction. These vary rapidly when the direction of the light rays traversing the plate is altered with reference to the plane of the laminations. To describe or discuss these effects in any detail would take us far beyond the scope of the present paper.

It seems fairly obvious that the laminated anisotropic structure of plate glass revealed by its optical behaviour is a consequence of the process employed in its manufacture. The molten glass emerges from the container in the furnace and passes between the forming rollers while it is still in a

plastic condition and becomes a sheet which moves on continuously until it finally sets and becomes solid. It is scarcely to be supposed that a sheet of glass formed under these dynamic conditions would possess the isotropic structure which is the ideal state of an amorphous solid. It appears much more probable that the movement of the layers of the material with respect to each other would result in the final product having a laminated structure, as is actually observed. The thickness of the laminæ would presumably be determined by the plasticity of the material and the speed of its passage through the rollers, as well as by their distance apart.

3. The Birefringence of Moulded Glass

The process employed for the mass production of objects of glass having a desired form is to use moulds. The glass is poured into the mould while in the fluid state and removed from it when it has solidified. Examination in polarised light of glass formed in this manner shows that the birefringence pattern which it exhibits bears a readily recognisable relationship to the geometric shape of the object. For instance, a circular disk of glass when viewed normally between crossed polaroids shows a dark cross which remains fixed when the disk is rotated in its own plane, the arms of the cross lying in the principal planes of the polariser and the analyser; the disk also exhibits a strong birefringence when held at an angle of 45° to these planes and viewed edgewise. A cube of moulded glass exhibits cubic symmetry in its birefringence, the pattern observed being the same whichever be the pair of faces through which it is viewed: the black cross seen is parallel to the edges of the cube in one symmetrical setting and to the face-diameters in another symmetrical setting, while in intermediate positions, the dark band seen takes the form of a swastika, the arms of which start at the face-centres and end at the face-corners. An equilateral prism of glass viewed through its end-faces shows trigonal symmetry in its optical behaviour; the birefringence pattern varies with the setting of the prism but repeats itself at regular intervals when the prism is rotated as required by such symmetry. Spheres and spheroids of moulded glass likewise exhibit the symmetry of their respective forms in their behaviour in respect of birefringence.

The foregoing statements, however, require to be qualified in an important respect. In every case, the geometric patterns implied by these descriptions are modified by the superimposition of a "structural birefringence" pattern. This consists of bright streaks traversing the glass block, their form and distribution bearing a recognizable relation to the shape of the block and being strongly suggestive of the shape of the flow lines of a viscous liquid enclosed within the walls of a mould of the concerned

geometric shape (see Plate XI). The structural birefringence in common glass has thus evidently a similar origin to that observed in the case of vitreous silica. The similarity of behaviour is even more vividly indicated by the photograph reproduced as Plate XII, which shows one of the flat walls of a large glass trough as viewed through a crossed pair of 6″ polaroids placed on either side of it.

The photographs reproduced in Plates XI, XII and XIII accompanying this paper were obtained by Mr. J. Padmanabhan, whose excellent assistance in the investigation I have much pleasure in acknowledging. Plate XIV is reproduced from material obtained during an unpublished research by Mr. Bawa Kanwal Singh, made at the author's suggestion.

Summary

The result reported in an earlier investigation with vitreous silica is now shown to be true also for other amorphous solids, including especially inorganic glasses; besides the well-known photo-elastic effect, another kind of birefringence may be observed differing from the former both in its origins and in its observable characters. This "structural birefringence" arises from anisotropy of structure present in the solid by reason of the circumstances of its formation. It is conspicuously seen with plate glass whose optical behaviour shows it to have a highly laminated structure, while in moulded glass, it exhibits itself as luminous streaks or sheets of variously curved forms.

Numerous photographs illustrate the paper.

Reference

Raman, C. V. .. *Proc. Ind. Acad. Sci.* **1950, 31A**, 141.

Description of the Figures

Plate XI. *Birefringence patterns seen between crossed polaroids*

Fig. 1. Cube of canary-yellow glass.

Figs. 2 & 3. Equilateral prism of glass in two different settings.

Fig. 4. Sphere of canary-yellow glass.

Figs. 5 & 6. Cube of glass cut from thick plate in two different settings.

Plate XII

Fig. 7. Part of one face of a large glass trough, seen through six-inch polariod sheets, crossed, set on either side of it.

PLATE XIII. *Plates viewed edgewise, between crossed polaroids*

FIG. 8. Quarter-inch thick glass plate, three inches wide.

FIG. 9. Same as Fig. 8 but with the quartz wedge superposed.

FIG. 10. Quarter-inch glass plate, $1\frac{1}{4}''$ wide.

FIG. 11. Same as Fig. 10 with quartz wedge superposed.

FIGS. 12 and 13; Same as Figs. 8 and 9, but showing free edge.

FIG. 14. One-eighth inch glass plate two inches wide.

FIG. 15. Same as Fig. 14 with quartz wedge superposed.

FIG. 16. One-sixteenth inch glass plate, $\frac{1}{2}''$ wide.

FIG. 17. Same as Fig. 16 with quartz wedge superposed.

FIG. 18. Quarter-inch plastic sheet, $3\frac{1}{2}''$ depth.

FIG. 19. Same as Fig. 18 with quartz wedge superposed.

PLATE XIV. *Photographs of glass block cut from thick plate*

FIG. 20. Showing the laminated structure of the block viewed in its plane.

FIG. 21. Same as Fig. 20, but with the block tilted slightly.

FIGS. 22–25. Glass block seen between crossed polaroids, in various settings, showing laminations.

FIGS. 26 & 27. Glass block with Babinet compensator fringes superposed obliquely, showing effect of the laminations.

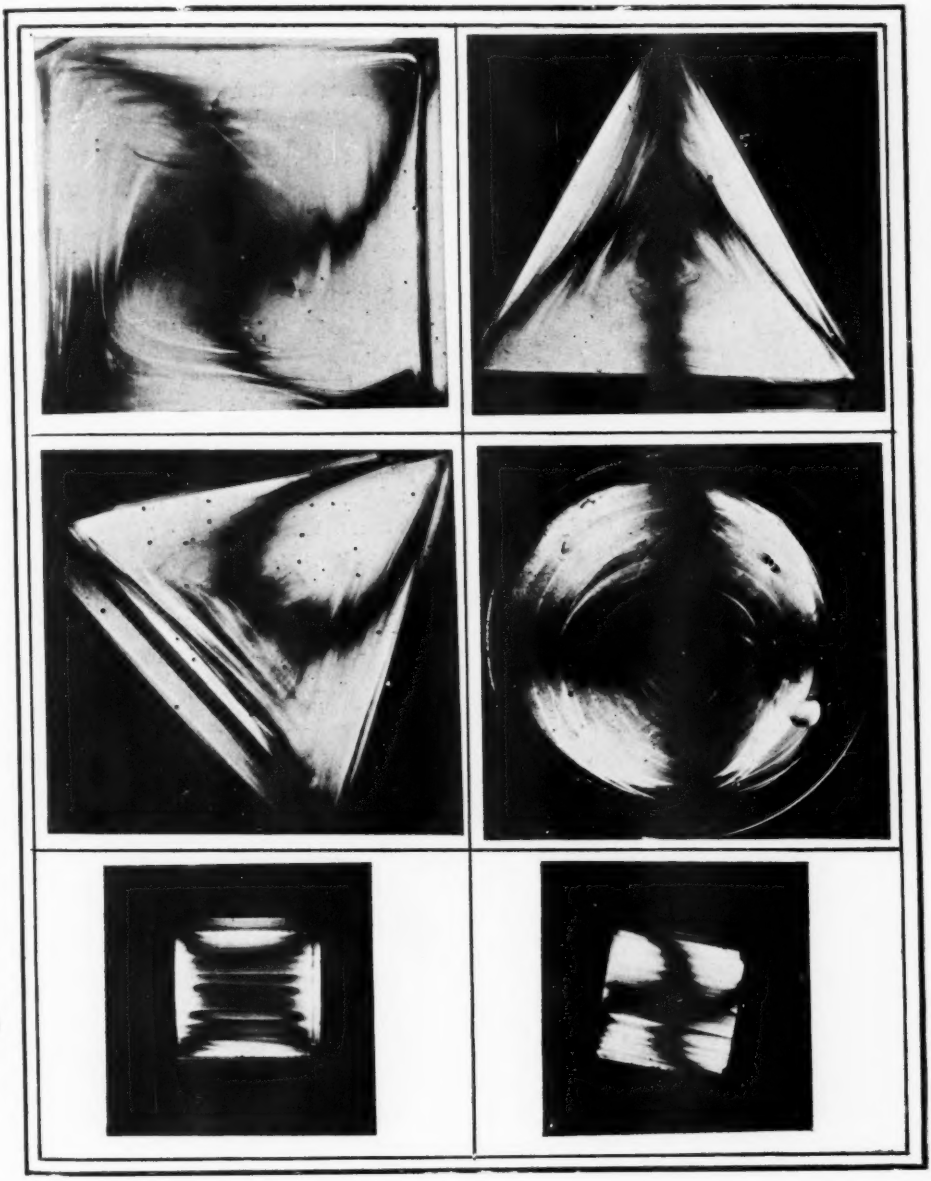

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

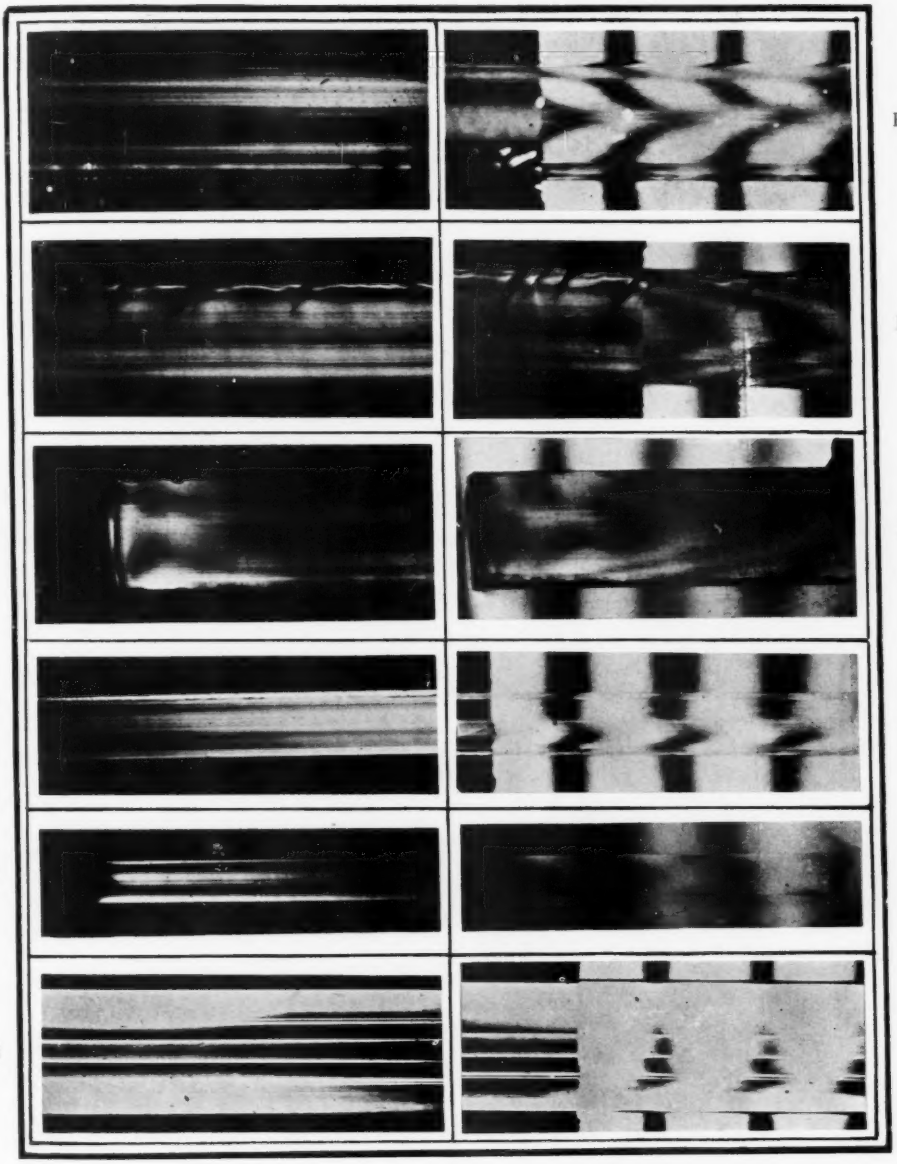

FIG. 3

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

FIG. 16

FIG. 17

FIG. 18

FIG. 19

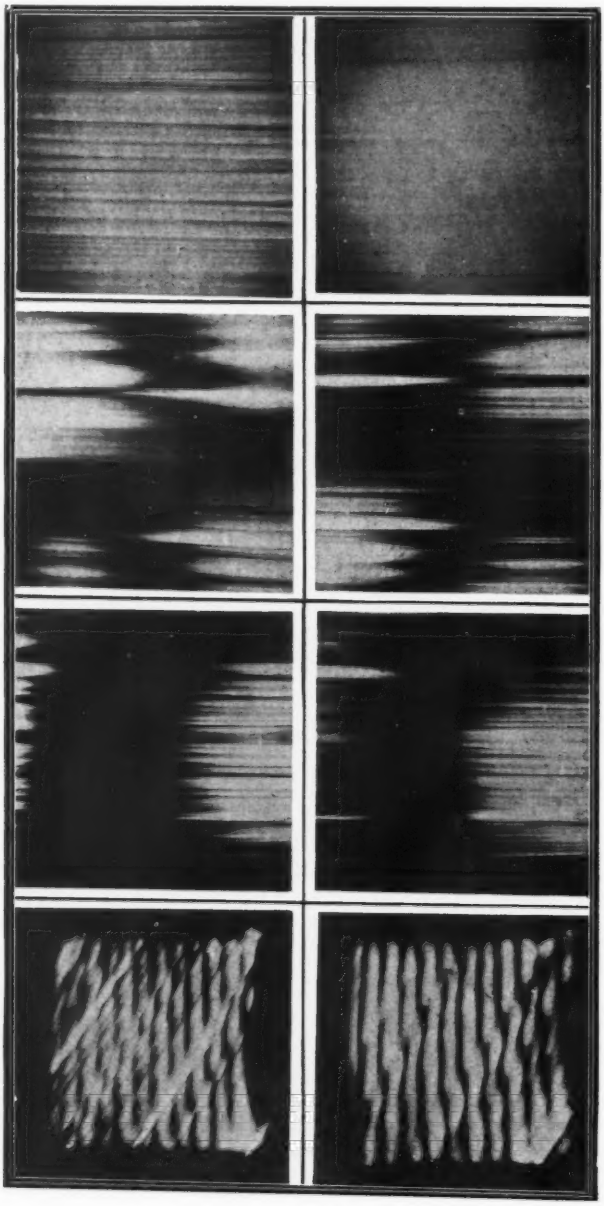

FIG. 20

FIG. 21

FIG. 22

FIG. 23

FIG. 24

FIG. 25

FIG. 26

FIG. 27

γ-SUBSTITUTION IN THE RESORCINOL NUCLEUS

Part VII. Fries and Friedel-Crafts Reactions of *o*- and *p*-Orsellinic Esters

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Received October 27, 1949

In the previous parts[1] it has been shown that the resorcinol nucleus which ordinarily reacts in the β-position, sometimes reacts in the γ-position, particularly when there is chelation due to the existence of a negative group in the β-position. In continuation of the above work, some reactions have now been studied in the case of orsellinic esters which are 5-methylresorcinol derivatives.

Orcinol is known to have a more marked tendency for γ-substitution than resorcinol. Thus, while on bromination,[2] Gattermann reaction[3] or Pechmann condensation with malic acid[4] substitution occurs in β-position; γ-substitution takes place on carboxylation,[5] condensation with acetic acid[6] or Pechmann condensation with ethyl acetoacetate.[7] On nitration,[8] nitrosation,[9] Reimer-Tiemann formylation[10] or Friedel-Crafts acetylation[11] both β- and γ-positions react.

Among the derivatives of orcinol, *o*-orsellinic acid and its esters are known to couple with diazonium salts in the β-position.[12] Gattermann reaction on ethyl *o*-orsellinate gives two products when zinc chloride is used as a condensing agent, the substitution occurring in both β- and γ-positions.[13] However, when the reaction is carried out in presence of aluminium chloride substitution takes place only in the γ-position.[14] Similar activation of γ-position in resorcinol derivatives in presence of aluminium chloride has already been noted in this laboratory.[1, 15]

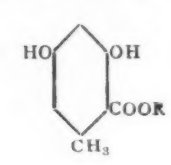
On Pechmann condensation ethyl *o*-orsellinate gives 5-hydroxy coumarin derivatives.[14] *p*-Orsellinic acid on similar condensation with ethyl acetoacetate gives 7-hydroxy-4: 5-dimethyl-8-carboxycoumarin.[16]

In the present work, Pechmann condensation of methyl *o*-orsellinate with ethyl acetoacetate and Fries and Friedel-Crafts reaction with methyl and ethyl esters of *o*- and *p*-orsellinic acids have been studied. The methyl and ethyl esters were prepared by the modified method of esterification described in the preceding paper.[17]

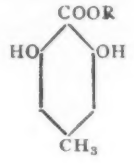
Pechmann condensation of methyl *o*-orsellinate (I, R=Me) with ethyl acetoacetate in presence of concentrated sulphuric acid gave *methyl 5-hydroxy-4: 7-dimethylcoumarin-6-carboxylate* (*III, R=Me*) in good yields (45-50%). The same product was obtained when the condensation was carried out in presence of phosphorus oxychloride or anhydrous aluminium chloride though in less yields (15-20%). With alkali it hydrolysed to an acid, m.p. 247°, which resembled in properties 5-hydroxy-4: 7-dimethylcoumarin-6-carboxylic acid (III, R=H) described by Sastry and Seshadri[14] and which on decarboxylation gave 5-hydroxy-4: 7-dimethylcoumarin.

The *diacetates* of methyl and ethyl esters of *o*- and *p*-orsellinic acids required for the Fries transformation were unknown and prepared by the usual methods.

On Fries transformation the diacetate of methyl *o*-orsellinate (I, R=Me) gave two products: one m.p. 99-100° (A) and another m.p. 99° (B), mixed m.p. of the two being depressed. The same two products were obtained on Friedel-Crafts reaction of methyl *o*-orsellinate with acetic anhydride or acetyl chloride. The diacetate of ethyl *o*-orsellinate (I, R=Et) on Fries rearrangement gave three products: an acid m.p. 151° (decomp.) (C), and two others, m.p. 86° (D) and m.p. 97° (E). However, only the last two products (D and E) were obtained on the Friedel-Crafts reaction of ethyl *o*-orsellinate with acetic anhydride or acetyl chloride.



(I)



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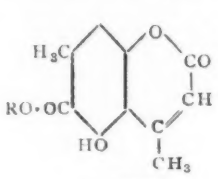

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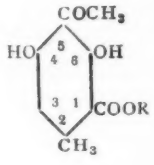

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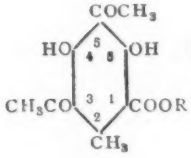

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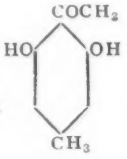

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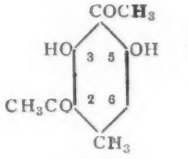

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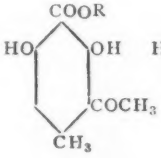

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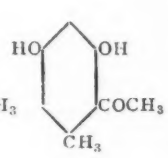

(IX)

All the products on boiling with alkali gave γ-orcacetophenone (VI). The products A, B, D and E appeared to be esters, but could not be hydrolysed to the corresponding acids. The acid (C) could be decarboxylated by copper quinoline method to give *2: 4-diacetylorcinol* (*VII*) and was therefore 3: 5-*diacetyl*-o-*orsellinic acid* (*V, R=H*). The acid (C) when esterified with

dimethyl sulphate in acetone solution in presence of sodium bicarbonate gave a methyl ester, identical with B. Hence B was *methyl* 3: 5-*diacetyl*-o-*orsellinate* (*V*, *R=Me*). The acid (C) similarly gave an ethyl ester which was found identical with E; the latter therefore, was *ethyl* 3: 5-*diacetyl*-o-*orsellinate* (*V*, *R=Et*). The products A (m.p. 99-100°) and D (m.p. 86°), could only be mono-substituted γ-acetyl derivatives and have hence been assigned the constitutions *methyl* 5-*acetyl*-o-*orsellinate* (*IV*, *R=Me*) and *ethyl* 5-*acetyl*-o-*orsellinate* (*IV*, *R=Et*) respectively.

Thus the Friedel-Crafts acetylation of *o*-orsellinic esters or the Fries transformation of their diacetates give both γ-acetyl and β: γ-diacetyl derivatives, namely, 5-acetyl and 3: 5-diacetyl-*o*-orsellininc esters. In the Fries transformation of the diacetate of the ethyl ester 3: 5-diacetyl-*o*-orsellinic acid (V, R=H) was obtained in addition.

For comparison Fries and Friedel-Crafts reactions were also carried out on methyl and ethyl *p*-orsellinates (II, R=Me and Et respectively). The *diacetates* of both these orsellinates on Fries transformation gave the same product, an acid m.p. 170° (decomp.). The same acid was obtained on Friedel-Crafts acetylation of methyl and ethyl *p*-orsellinates, but in better yields. The acid underwent decarboxylation when heated with copper-quinoline to give β-orcacetophenone (IX) and was therefore *3-acetyl*-p-*orsellinic acid* (*VIII*, *R=H*). It was also prepared from β-orcacetophenone by carboxylation with potassium bicarbonate in glycerine. It may be noted that in this case, as also in orcinol, the carboxyl group enters in the γ-position. Further, when the γ-position is not free, such as in γ-orcacetophenone, such carboxylation could not be carried out.

Attempts were made to introduce another acetyl group, by carrying out Friedel-Crafts reaction on *methyl 3-acetyl*-p-*orsellinate* (*VIII*, *R=Me*) with acetic anhydride on acetyl chloride and also by Fries transformation of its *diacetate*. However only de-esterification occurred and 3-acetyl-*p*-orsellinic acid (VIII, R=H) was obtained.

An interesting point observed is the easy elimination of the β-acetyl group in orcinol derivatives. As already stated 3: 5-diacetyl-*o*-orsellinic acid as well as its methyl and ethyl esters on boiling with alkali give γ-orcacetophenone (VI). 2: 4-Diacetylorcinol (VII) has been also found to behave similarly (*cf.* Desai and Mavani[18]). Further during the carboxylation of β-orcacetophenone (IX), it was observed that if higher temperatures were used de-acetylation occurred giving *p*-orsellinic acid (II, R=H). Desai and Ekhlas[19] and Shah and Shah[20] have also made similar observations during the Pechmann condensation of β-orcacetophenone.

In the esters of *o*-orsellinic acid the γ-reactivity is exhibited to a greater extent. Thus on Friedel-Crafts acetylation of *o*-orsellinic esters, the mono-substitution occurs exclusively in the γ-position. In the corresponding resorcinol derivative, namely, methyl β-resorcylate, Dsesai and Ekhlas[21] have observed the formation of β-substituted derivative during Friedel-Crafts acylation. Recently Trivedi and Sethna,[22] however, have shown that the γ-isomer is also formed in substantial amount simultaneously. Further, Pechmann condensation of methyl *o*-orsellinate with ethyl acetoacetate in presence of concentrated sulphuric acid or phosphorus oxychloride gives 5-hydroxycoumarin derivative, substitution occurring in the γ-position. Methyl β-resorcylate however, under similar conditions, gives the corresponding 7-hydroxy coumarin derivatives,[23] although in the presence of aluminium chloride 5-hydroxycoumarin derivatives are formed.[15] The exclusive γ-reactivity observed in the present case in the *o*-orsellinic esters can be considered as due to the abnormal γ-reactivity of the orcinol nucleus.

In the case of *p*-orsellinic esters, as the γ-position is occupied, the substitution as would be expected, occurs in one of the two β-positions.

Experimental

Pechmann Condensation of Methyl o-*Orsellinate with Ethyl Acetoacetate: Methyl 5-Hydroxy-4: 7-dimethylcoumarin-6-carboxylate* (*III*, $R = Me$)

1. To a cooled mixture of methyl *o*-orsellinate[17] (m.p. 138°) (2 g.) and ethyl acetoacetate (2·4 c.c.) cooled in ice, concentrated sulphuric acid (4·0 c.c.) was added and the mixture was kept overnight. The next day it was diluted with ice-water and the product collected, washed and crystallised from rectified spirit, when *methyl 5-hydroxy-4: 7-dimethyl-coumarin-6-carboxylate* (*III*, $R = Me$) separated in colourless needles, m.p. 195-96° (yield 45%) (Found: C, 62·7; H, 5·1; $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·8%). It gave a purple-violet coloration with alcoholic ferric chloride, and slowly dissolved in dilute alkali with a yellow coloration.

2. When the condensation was carried out in presence of phosphorus oxychloride (0·5 c.c.) by heating it with a mixture of methyl *o*-orsellinate (2 g.) and ethyl acetoacetate (1·4 c.c.) on a steam-bath for one and half hours to two hours and extracting the cooled reaction mixture with benzene, the same product, m.p. 195-96°, after crystallisation, was obtained (yield 15-20%).

3. Methyl *o*-orsellinate (2 g.) and ethyl acetoacetate (1·4 c.c.) in nitrobenzene and anhydrous aluminium chloride (6 g.) in nitrobenzene were mixed and heated at 120-30° for one hour. It was cooled, ice and

hydrochloric acid added and nitrobenzene removed by steam-distillation. After crystallisation from rectified spirit (charcoal), the same product, m.p. 195-96° was obtained (yield 15-20%).

5-Hydroxy-4: 7-dimethylcoumarin-6-carboxylic acid (III, R = H)

The coumarin ester (1 g.) obtained above, when kept with potassium hydroxide (5%; 10 c.c.) for 30 hours at room temperature, and then neutralised the solution with dilute hydrochloric acid (1 : 1) gave 5-hydroxy-4: 7-dimethylcoumarin-6-carboxylic acid (III, R = H) crystallised from rectified spirit, tiny white needles, m.p. 248° (Sastry and Seshadri[14]; m.p. 248°). It gave a violet colouration with alcoholic ferric chloride.

5-Hydroxy-4: 7-dimethylcoumarin

The above coumarin acid (0·25 g.) was dissolved in sufficient quinoline and heated at 170° with copper-bronze for one hour. The mixture was dissolved in excess of ether, filtered, ether evaporated and residue treated with dilute hydrochloric acid. The precipitate was collected, washed and crystallised from rectified spirit, tiny colourless needles of 5-hydroxy-4: 7-dimethyl coumarin, m.p. and mixed m.p. with an authentic specimen from orcinol, 258° (Sastry and Seshadri[14]; m.p. 258°).

Diacetate of Methyl o-Orsellinate (Methyl 4: 6-Diacetoxy-2- methylbenzoate).

Methyl *o*-orsellinate (10 g.) was refluxed with acetic anhydride (15 c.c.) and pyridine (5 drops) for two hours and the reaction mixture was worked up in the usual manner. The crude product was dissolved in ether and little light petroleum added when after keeping for sometime in frigidaire, the diacetate separated in colourless needles, m.p. 55° (2 g.) (Found: C, 58·9; H, 5·1. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%.) It did not give coloration with alcoholic ferric chloride.

Fries Transformation of the Diacetate of Methyl o-Orsellinate: Methyl 5-Acetyl-o-orsellinate (IV, R = Me) and Methyl 3: 5-Diacetyl-o-orsellinate (V, R = Me)

The diacetate (0·5 g.) was intimately mixed with powdered aluminium chloride (1·2 g.; 2·2 mols) and heated at 100° for one and half hours. It was cooled, treated with ice and concentrated hydrochloric acid. It was then extracted with ether and the extract washed repeatedly with bicarbonate solution. Nothing was obtained on working up the ether extract. The bicarbonate solution, after acidification, extraction with ether and working up the ether extract gave a product which was crystallised from methanol, transparent needles, m.p. 100° (B) (Found: C, 58·8; H, 5·2. $C_{13}H_{14}O_6$

requires C, 58·6; H, 5·3%). It was found to be *methyl* 3: 5-*diacetyl*-o-*orsellinate* (*V*, *R* = *Me*) as it did not depress the mixed melting point of an authentic specimen prepared as described later (*v. infra*). The ester was recovered unchanged when kept with sodium hydroxide (2N) or alcoholic potassium hydroxide for 48 hours. However, when boiled with sodium hydroxide (1N) for one hour, γ-orcacetophenone,[6] m.p. and mixed m.p. 146°, was obtained. *Oxime* of methyl 3: 5-diacetyl-*o*-orsellinate was crystallised from dilute methanol, colourless needles, m.p. 185° (Found: N, 9·4, $C_{13}H_{16}O_6N_2$ requires N, 9·5%).

When the experiment was repeated using 3·3 mols of anhydrous aluminium chloride (1·8 g.), along with traces of the above product (B), another product which was insoluble in bicarbonate and remained in ether extract, was obtained. It was crystallised from methanol, colourless needles, m.p. 101° (A) whose mixed melting point with the above product (B) was considerably depressed. As the corresponding 3: 5-diacetyl derivative (V, R = Me), this (A) also could not be hydrolysed to the acid (IV, R = H) on keeping with alkali at room temperatures, and at higher temperatures gave γ-orcacetophenone, m.p. 146°, decarboxylation occurring simultaneously. Hence it has been assigned the constitution *methyl* 5-*acetyl*-o-*orsellinate* (*IV*, *R* = *Me*) (Found: C, 58·7; H, 5·3. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%). Attempts were made to prepare the corresponding acid (IV, R = H) by heating γ-orcacetophenone (VI, 0·5 g.), potassium bicarbonate (1 g.) and anhydrous glycerine (1 c.c.) in a current of carbon dioxide at various temperatures. Most of the original ketone was recovered with traces of an oily product, showing acidic properties.

The Fries transformation of the diacetate (1 g.) when carried out in nitrobenzene (2 c.c.) with anhydrous alluminium chloride (0·6 g.; 1·1 mol.), methyl 5-acetyl-*o*-orsellinate (IV, R = Me) (0·3 g) and small quantity of methyl 3: 5-diacetyl-*o*-orsellinate (V, R = Me) were obtained.

Friedel-Crafts Reaction on Methyl o-*Orsellinate with Acetic Anhydride and Acetyl Chloride*: *Methyl* 5-*Acetyl*-o-*orsellinate* (*IV*, *R* = *Me*) *and Methyl* 3: 5-*Diacetyl*-o-*orsellinate* (*V*, *R* = *Me*)

To a cooled solution of aluminium chloride (1·1 g.; 2·9 mol.) in nitrobenzene were added methyl *o*-orsellinate (0·5 g.) and acetic anhydride (0·5 c.c.; 1·5 mol.). After keeping it overnight at room temperature it was gradually heated to 100° and kept for 45 minutes at this temperature. The temperature was then raised to 120°, heating discontinued, cooled and ice and hydrochloric acid added. After removal of nitrobenzene by steam distillation, the residual solution was extracted with ether, the extract washed

with bicarbonate solution, dried and ether removed, when methyl 5-acetyl-*o*-orsellinate (IV, R = Me), m.p. 100° was obtained.

When the reaction was carried out with excess of acetic anhydride (2·5 mols.) or acetyl chloride (3 mols.) and aluminium chloride mainly methyl 3:5-diacetyl-*o*-orsellinate (V, R = Me), m.p. 99-100°, was obtained from the bicarbonate washing, along with traces of methyl 5-acetyl-*o*-orsellinate (IV, R = Me).

Fries Transformation of Diacetate of Ethyl o-Orsellinate (Ethyl 4:6-*Diacetoxy*-2-*methylbenzoate*): 3:5-*Diacetyl*-o-*orsellinic Acid* (*V, R = H*), *Ethyl* 5-*Acetyl*-o-*orsellinate* (*IV, R = Et*) *and Ethyl* 3:5-*Diacetyl*-o-*orsellinate* (*V, R = Et*)

The diacetate of ethyl *o*-orsellinate[17] (prepared in the same way as that of the methyl ester, m.p. 42°) (1 g.) was mixed with powdered anhydrous aluminium chloride (1·6 g.; 2·2 mol.) and heated for one and half hours. It was worked up as in the previous case. The ether extract was washed with bicarbonate solution. Nothing could be obtained from the ether extract. The bicarbonate washing after acidification, extraction with ether and working up the ether extract gave an acid, crystallised from acetic acid, needles, m.p. 151° (efferv.) (C). It gave on decarboxylation 2:4-diacetylorcinol,[20] m.p. and mixed m.p. 96° and was therefore 3:5-*diacetyl*-o-*orsellinic acid* (*V, R = H*) (Found: C, 57·0; H, 4·9. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8%). Methyl ester (V, R = Me), prepared by the bicarbonate method,[17] and crystallised from methanol m.p. 99-100°. It did not depress the melting point of the diketonic product obtained from Fries transformation of the diacetate of methyl *o*-orsellinate. *Ethyl ester* (*V, R = Et*), prepared similarly[17] and crystallised from methanol needles, m.p. 96-7° (Found: C, 59·6; H, 5·3. $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·7%).

When the experiment was carried out in nitrobenzene two products were obtained: (1) one insoluble in bicarbonate solution and remaining in ether, crystallised from methanol, m.p. 87° (D), and (2) another soluble in bicarbonate, crystallised from methanol, m.p. 97° (E). Both the products like those from the corresponding methyl ester, could not be hydrolysed to the corresponding acid, and on boiling with alkali gave γ-orcacetophenone (VI). The product, m.p. 97° (E), was identical with the ethyl ester mentioned above and was therefore ethyl 3:5-diacetyl-*o*-orsellinate (V, R = Et). The other product, m.p. 87° (D), has been assigned the constitution *ethyl* 5-*acetyl*-o-*orsellinate* (*IV, R = Et*) (Found: C, 60·6; H, 6·0, $C_{12}H_{14}O_5$ requires C, 60·6; H, 5·9%).

Friedel-Crafts Reaction on Ethyl o-*Orsellinate with Acetic Anhydride and Acetyl Chloride: Ethyl* 5-*Acetyl*-o-*orsellinate* (*IV*, *R* = *Et*) *and Ethyl* 3:5-*Diacetyl*-o-*orsellinate* (*V*, *R* = *Et*)

Ethyl *o*-orsellinate (0·5 g.) and acetic anhydride (0·4 c.c.; 1·5 mol.) were added to a cooled solution of anhydrous aluminium chloride (0·9 g.; 2·9 mol.) in nitrobenzene, and the reaction mixture kept overnight at room temperature. The next day it was heated at 100° for about an hour, and worked up as before. The ether extract taken after removal of nitrobenzene was washed with bicarbonate solution and worked up when ethyl 5-acetyl-*o*-orsellinate (IV, R = Et), m.p. 87°, was obtained.

When the reaction was conducted with excess acetic anhydride (2·5 mols.) mainly ethyl 3:5-diacetyl-*o*-orsellinate (V, R = Et), m.p. 97°, was obtained together with ethyl 5-acetyl-*o*-orsellinate (IV, R = Et), m.p. 87°. When acetyl chloride (3 mols.) was used only the former product (V, R = Et) was obtained.

2:4-*Diacetylorcinol* (*VII*)

Desai and Mavani[18] prepared it by the Fries transformation of orcinol diacetate. However, no experimental details are available. In the present case it has been prepared from the diacetate by similar method. Orcinol diacetate (colourless oil, b.p. 240°/10 mm.) (6 g.) and powdered anhydrous aluminium chloride (12 g.) were heated at 150° for 2 hours. After cooling ice and hydrochloric acid were added and the product collected, washed and crystallised from dilute acetic acid, when 2:4-diacetylorcinol separated in pale yellow needles, m.p. 96° (2·5 g.). (Found: C, 63·7; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%.)

It gets deacetylated when kept with concentrated sulphuric acid or when boiled with alkali solution (1 N) for one hour giving γ-orcacetophenone (VI), m.p. 146°. Raisinki[6] gives the same melting point.

Fries Transformation of the Diacetate of Methyl p-*Orsellinate* (*Methyl* 2:6-*Diacetoxy*-4-*methylbenzoate*): 3-*Acetyl*-p-*orsellinic Acid* (*VIII*, *R* = *H*)

The *diacetate* of methyl *p*-orsellinate was prepared by refluxing the latter (II, R = Me; m.p. 99°)[17] (2 g.) with acetic anhydride (3 c.c.) and pyridine (4 drops) for two hours and working up as usual. The crude product was dissolved in ether and little light petroleum added and kept in a freezing mixture when transparent needles of the diacetate separated, m.p. 70° (2 g.) (Found: C, 58·2; H, 5·5. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%).

The diacetate (0·5 g.) was intimately mixed with powdered aluminium chloride (0·9 g.; 3·3 mol.) and heated at 100° for one and half hours. It was cooled, ice and hydrochloric acid added and worked up as before. The product separated, was crystallised from dilute methanol (50%), transparent needles, m.p. 170° (efferv.) (0·1 g.). When heated with copper and quinoline it got decarboxylated giving β-orcacetophenone (IX), m.p. and mixed m.p. 158°, with an authentic specimen obtained by Hoesch reaction.[24] Hence the product was 3-*acetyl*-p-*orsellinic acid* (*VIII*, $R = H$) (Found: C, 57·2; H, 4·7. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8%).

When the reaction was carried out in nitrobenzene, the same product m.p. 170° (efferv.) was obtained.

Friedel-Crafts Reaction on Methyl p-*Orsellinate* (*II*, $R = Me$) *with Acetic Anhydride:* 3-*Acetyl*-p-*orsellinic Acid* (*VIII*, $R = H$)

To a cooled solution of anhydrous aluminium chloride (1·05 g.; 2·85 mols.) in nitrobenzene (4 c.c.) were added methyl *p*-orsellinate (0·5 g.) and acetic anhydride (0·45 c.c.; 1·5 mol.) and kept overnight at room temperature. Next day it was heated at 100° for one and half hours and then at 120-25° for 15 minutes, cooled, ice and concentrated hydrochloric acid added and worked up as usual when on crystallisation from methanol (50%) 3-acetyl-*p*-orsellinic acid, m.p. 170°, was obtained.

Experiment was repeated with excess acetic anhydride (2·5 mols.) but the same product was obtained.

Fries Transformation of Diacetate of Ethyl p-*Orsellinate and Friedel-Crafts Reaction on Ethyl* p-*Orsellinate with Acetic Anhydride:* 3-*Acetyl*-p-*orsellinic Acid* (*VIII*, $R = H$)

The diacetate of ethyl *p*-orsellinate was prepared from the latter[17] (II, R = Et; m.p. 62°) in the same way as the corresponding one from methyl ester, and was obtained as an oil which did not solidify on keeping and did not give ferric chloride coloration. The oil was used directly for migration.

To the diacetate (0·5 g.) was added powdered aluminium chloride (0·8 g.) and the mixture heated at 100° for one and half hours, cooled, ice and hydrochloric acid added and worked up as usual, when on crystallisation 3-acetyl-*p*-orsellinic acid (VIII, R = H), m.p. 170°, was obtained. The same product was obtained when nitrobenzene was used as a solvent.

The Friedel-Crafts reaction was carried out as in the previous case with ethyl *p*-orsellinate (0·5 g.), anhydrous aluminium chloride (0·9 g.;

2·8 mols.) in nitrobenzene (2 c.c.) and acetic anhydride (0·4 c.c.; 1·5 mol.) when the same product, m.p. 170° (VIII, R = H) was obtained. Use of excess of acetic anhydride (2·5 mols.) also gave the same result.

*Carboxylation of β-Orcacetophenone (IX): 3-Acetyl-*p*-orsellinic Acid (VIII, R = H)*

β-Orcacetophenone (0·5 g.), dry potassium bicarbonate (1 g.) and anhydrous glycerine (1 c.c.) were heated in a current of carbon dioxide at 100-05° for 5 hours. It was diluted with water, acidified, and the product crystallised from dilute acetic acid, needles, m.p. 170° (efferv.). When the carboxylation was attempted at 140-50°, deacetylation occurred affording *p*-orsellinic acid. *Methyl ester (VIII, R = Me)* prepared by the bicarbonate method, crystallised from alcohol (50%) white needles, m.p. 94-95° (Found: C, 58·3; H, 5·2. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%). The diacetate of the methyl ester, m.p. 72-73°.

Attempted Fries transformation of the above diacetate or Friedel-Crafts reaction on methyl ester (VIII, R = Me) with acetic anhydride gave only 3-acetyl-*p*-orsellinic acid (VIII, R = H).

Summary

In continuation of the previous work on γ-substituiton in resorcinol nucleus, substitution is studied in the derivatives of orcinol which is known to show 'abnormal' γ-reactivity. On Pechmann condensation with ethyl aceto-acetate methyl *o*-orsellinate gave methyl 5-hydroxy-4: 7-dimethyl-coumarin-6-carboxylate. Friedel-Crafts reaction on methyl *o*-orsellinate with acetic anhydride or acetyl chloride and Fries reaction of its diacetate gave two products: methyl 5-acetyl-*o*-orsellinate and methyl 3: 5-diacetyl-*o*-orsellinate. The diacetate of ethyl *o*-orsellinate gave on Fries transformation the corresponding ethyl esters of the above two products along with 3: 5-diacetyl-*o*-orsellinic acid; while the Friedel-Crafts acetylation gave only the first two products. Friedel-Crafts reaction on methyl and ethyl *p*-orsellinates and Fries reaction of their diacetates gave 3-acetyl-*p*-orsellinic acid.

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TEMPERATURE VARIATION OF THE REFRACTIVE INDEX OF LITHIUM FLUORIDE

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1. Introduction

Lithium fluoride is the most transparent of all solids to the ultra-violet, and possesses considerable infra-red transparency as well. Its refractive index has been measured practically over the whole range of transmission (Gyulai, 1927; Schneider, 1936; Hohls, 1937) and can be accurately expressed by means of a dispersion formula (Radhakrishnan, 1948). But measurement of the variation of refractive index with temperature seems to have been confined to an isolated observation by Hohls, on the refractive indices at 18° C. and 80° C. for two wavelengths, 5461 Å and $3{\cdot}5\mu$. In view of this fact, the author has undertaken a detailed determination of the temperature coefficients dn/dt from 0° C. to 400° C. for the wave-lengths 4358 and 5461 Å of mercury and 5893 Å of sodium. Modern ideas of thermo-optic behaviour, applied to these experimental values, furnish quantitative information regarding the influence of temperature on the electronic characteristic frequency of lithium fluoride.

2. Experimental Technique

An interferometric method, which had already been used in this laboratory by Ramachandran for diamond (1947) and by Radhakrishnan for quartz (1947) was adopted in the present case. The detailed description of the technique is contained in these papers and is therefore not repeated here. The following modifications, however, were effected for the measurements with lithium fluoride.

The clear, strain-free specimen of lithium fluoride, ($10 \times 5 \times 1$ mm.), gave after grinding and polishing parallel to a cubic plane a system of circular localised fringes. These fringes did not sharpen up (unlike in the previous cases of diamond and quartz) on coating both sides with aluminium and observing the transmitted system. Hence the reflected system was used.

This was obtained in the usual manner by reflecting monochromatic light normally on the crystal from a small aperture by means of a rigidly fixed glass plate. A light coat of aluminium on the glass plate improved the observed intensity of the fringe system for obvious reasons.

The mounting of the crystal and observation of the fringe shifts were carried out in the usual manner (Radhakrishnan, 1947). But the determination of the temperature change between successive shifts was improved by rendering it uniformly accurate over the whole temperature range studied. This was done by sending into the galvanometer an e.m.f. equal and opposite to that of the thermocouple every time the deflection came to the end of the scale, and thereby reducing the deflection to zero value without altering the sensitiveness. The resistances of the thermocouple circuit and the 'compensating circuit' were arranged to be very large compared to that of the galvanometer (which was a 450 Ω mirror instrument, shunted by 0·2 Ω). Under these conditions the galvanometer deflections were directly proportional to the difference in e.m.f.'s between the two circuits. The temperature interval between two successive fringe shifts did not alter much at any part of the range studied. This fact greatly increased the accuracy of the determinations.

To extend the readings below room temperatures, the low temperature 'Dewar flask' (Radhakrishnan, 1947) was used. But the rate of heating and cooling of the container was too rapid for the crystal to follow so that reliable measurements could be pushed down only to 0° C. The wave-lengths used were λ4358 and λ5461 of the mercury arc and λ5893 of the sodium lamp.

3. Results

From the observations described above, (dn/dt) was calculated by means of the relation

$$\frac{dn}{dt} = \frac{\lambda}{2l}\frac{1}{\Delta t} - n\alpha, \tag{1}$$

where l is the crystal thickness, Δt the difference in temperature between successive fringe shifts calculated as an average over six fringe shifts about the mean temperature, λ the wave-length of the light and α the linear expansion which was calculated from the formula of Eucken and Danöhl (1934):—

$$\alpha_t = 0{\cdot}0_5 3317 + 0{\cdot}0_8 3075t + 0{\cdot}0_{11} 2399t^2 \tag{2}$$

The values of dn/dt are displayed in Table I. The absolute values are probably correct within five units in the last decimal place, while the dispersion of dn/dt is correct within two units.

TABLE I

Mean Temp. (deg. C.	$10^5\alpha$	$-10^5 \frac{dn}{dt}$		
		4358	5461	5893
0	3·317	1·28	1·30	1·31
100	3·644	1·67	1·69	1·68
200	4·024	2·00	2·00	2·00
300	4·452	2·49	2·51	2·51
400	4·928	2·94	2·95	2·96

4. DISCUSSION

It is seen that the temperature coefficients are negative and vary considerably with temperature and very little with wave-length. To explain these features quantitatively, we consider the dispersion formula of lithium fluoride (Radhakrishnan, 1948):—

$$n^2 = 1\cdot34880 + \frac{0\cdot57862\,\lambda^2}{\lambda^2 - 0\cdot00814} + \frac{7\cdot34258\,\lambda^2}{\lambda^2 - 1106\cdot6} \tag{3}$$

This two-term formula incorporates an ultra-violet absorption at 900 Å and the observed infra-red absorption at 33 μ. For our purpose, we write this in the frequency form:—

$$n^2 = a + \frac{b}{\nu_0^2 - \nu^2} - \frac{c}{\nu^2} \tag{4}$$

where

$$a = 1\cdot34880,\quad b = 71\cdot11,\quad \nu_0 = 122\cdot8 \text{ and } \quad c = 0\cdot0067.$$

The excess over unity in a is due to the presence of ultra-violet absorptions which are so remote that their contribution to n remain sensibly constant over the range of transmission of the crystal. Similarly the remoteness of the infra-red frequency justifies its replacement by a term $-\frac{c}{\nu^2}$ right up to the red end of the visible region.

As the crystal is heated, the change in its refractive index is due to (1), the decrease in oscillator strengths b, c, etc., which is proportional to the decrease in density of the crystal, and (2) the change in polarisability of the crystal which can be pictured as a shift in the absorption frequencies ν_r. Ramachandran (1947) has given a general expression connecting these

changes. In the case of lithium fluoride considerable simplification is possible, since the infra-red term is so remote that any shift in its frequency will not affect dn/dt, while the ultra-violet terms reduce to just one, namely that due to the frequency at 900 A. The remote ultra-violet frequency will not change with temperature. Bearing these in view, Ramachandran's equation can be written for lithium fluoride in the form

$$\frac{dn}{dt} = -\gamma_t \frac{n^2-1}{2n} + \frac{1}{2n} \frac{2b\nu_0^2 \chi_t}{(\nu_0^2 - \nu^2)^2} \tag{5}$$

where χ_t is defined by the relation

$$-\chi_t = \frac{1}{\nu_0} \frac{d\nu_0}{dt} \tag{6}$$

and γ_t is the coefficient of cubical expansion of the crystal at that temperature, that is, $3\alpha_t$. In equation (5) all quantities are known except χ. The solution of χ after substituting numerical values gives

$$\chi_t = \begin{Bmatrix} 2{\cdot}27\left[\left(\frac{dn}{dt}\right)_{5461} + 1{\cdot}01\ \alpha\right] \\ 2{\cdot}20\left[\left(\frac{dn}{dt}\right)_{4358} + 1{\cdot}02\ \alpha\right] \end{Bmatrix} \tag{7}$$

The solution for λ5893 is omitted since it is practically the same as that for λ5461. The values of χ_t obtained in this manner are set out in Table II.

TABLE II

Temperature (deg. C.)	$10\chi^5_t$	
	4358	5461
0	4·65	4·65
100	4·50	4·54
200	4·60	4·61
300	4·55	4·45
400	4·60	4·54

The sign and magnitude of χ are similar to what is found in most crystals (*e.g.*, fluorite, $\chi = 3{\cdot}3 \times 10^{-5}$). The results indicate that over the region of temperature investigated χ does not exhibit any appreciable variation with temperature, as in the case of fluorite. The χ value is sufficiently high to offer quite a large contribution to dn/dt, and it occurs in combination

with a term $1/(\nu_0^2 - \nu^2)^2$ (Equation 5), which varies rapidly with wave-length. Nevertheless, it is seen that dn/dt varies very little with wave-length. This is because of the remoteness of the ultra-violet frequency ν_0, owing to which the variation in the volume term $-\gamma (n^2 - 1)/2n$ almost cancels the variation in the term containing χ_t. If we could extend the measurements to the ultra-violet, however, we would find that the χ term is the factor which chiefly determines the dispersion of dn/dt at low wave-lengths.

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Summary

The thermal variation of the refractve index of lithium fluoride has been measured from 0° C. to 400° C. for λ4358, 5461 and 5893, and the dependence on temperature of the electronic characteristic frequency of the crystal has been computed therefrom.

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THE REFRACTION OF MAGNESIUM OXIDE AND ITS TEMPERATURE VARIATION

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1. Introduction

Magnesium oxide crystallises in the cubic system, the natural mineral being known as β-magnesia or periclase. Large synthetic crystals of magnesia are being manufactured nowadays, because its refractory properties render it of great importance in ceramics, and its optical quality and resistivity to corrosion make it useful for the construction of optical instruments. For these same reasons, the thermal expansion and optical properties of magnesia have been thoroughly studied. Thilenius and Holzmann (1930) have determined the linear expansion coefficient with great precision from 20° C. to above 2000° C. Strong and Brice (1935) have examined the transmission in the ultra-violet and determined the refractive indices from 2536 Å to 7065 Å. Barnes, Brattain and Seitz (1935) have measured the infra-red absorption and reflection and calculated therefrom the refractive index in the infra-red. Recently, measurements of the photo-elastic constants have also appeared (Burstein and Smith, 1948). From the photoelastic constants, Burstein and Smith have evaluated the variation of refractive index with density, $dn/d\rho$. They find that this coefficient is negative, *i.e.*, the refractive index decreases under hydrostatic pressure. This behaviour of magnesium oxide is unique, all other crystals so far studied showing a positive $dn/d\rho$. Burstein and Smith predict on this basis that magnesium oxide should have a positive temperature coefficient of refractive index, dn/dt. Measurements by Strong and Brice (1935) of the refractive indices at 23° C. and 2° C. seem to support this view. To confirm it in a more precise fashion and to gain further information about the effect of temperature on the optical properties of the crystal, the author has measured the temperature coefficient of the refractive indices for λ 4358, λ 5461 and λ 5893 from room temperature to 400° C. These values have been examined in the light of a dispersion formula for magnesium oxide computed by the author from Strong and Brices' data for the refractive indices. Several interesting points arise from these calculations.

2. The Refraction of Magnesium Oxide

The measurements of the refractive indices made by Strong and Brice are given to four decimal places from 2536 Å till the visible region, and thereafter to five places till 7065 Å. The refractive indices in the infra-red region have been calculated from measurements of the reflecting power (Barnes, Brattain and Seitz, 1935); but their values disagree totally with those of Strong and Brice at the red end. Consequently, the author has constructed a dispersion formula which does not take into account the contributions to dispersion from infra-red frequencies. This formula employs only a single ultra-violet term at 1180 Å and is likely to present a rather over-simplified picture. It is perhaps because of this that the formula shows signs of failing at 2536 Å, the lowest wave-length studied. Nevertheless, it can be used with confidence throughout the visible region. It was not found necessary to employ a small correction term for infra-red absorption even at 7065 Å. This suggests that the infra-red absorptions effective in refraction are very remote and their contributions to the refractive index are negligible throughout the visible region. Likewise, there will be absorption frequencies in the remote ultra-violet due to electronic transitions between purely atomic levels, which offer practically constant contributions to n^2. These constants are contained in the first term a which is greater than the theoretical value of unity given by the Drude formula. The formula and its agreement with the existing data are shown below:—

$$\left.\begin{aligned} M^2 &= a + b/(\nu_0^2 - \nu^2), \\ &= a + b'\lambda^2/(\lambda^2 - \lambda_0^2) \end{aligned}\right\} \qquad (1)$$

where $a = 1{\cdot}3224$, $b = 117{\cdot}48$, $\nu_0^2 = 72{\cdot}098$, $\nu = 1/\lambda$ in microns;

$b' = 1{\cdot}6294$, $\lambda_0^2 = 0{\cdot}01387$, λ being in microns.

Table I

λ(Å.u.)	n(Calculated)	n(Observed)
2536	1·8438	1·8450
2967	1·8046	1·8046
3128	1·7947	1·7945
3658	1·7721	1·7720
4046	1·7613	1·7613
4358	1·7551	1·7551
4861	1·7473	1·7474
5461	1·7411	1·7412
5893	1·7377	1·7379
6563	1·7339	1·7336
7065	1·7316	1·7313

3. The Temperature Coefficient of Refraction

The temperature variation of the refractive index was measured by the same interference method as was employed by the author for measurements with lithium fluoride (Radhakrishnan, 1950). The specimen of magnesia used was clear and strain-free (dimensions $7 \times 5 \times \cdot 95$ mm.), and was ground and polished parallel to a cubic face.

The values of dn/dt obtained with this specimen are given in Table II, the thermal expansion coefficients being taken from the work of Thilenius and Holzmann (1930).

Table II

Temperature (deg. C.)	Linear expansion $10^5\alpha$	$10^5\, dn/dt$		
		4358	5461	5893
65	1·13	1·79	1·65	1·56
145	1·19	1·80	1·64	1·55
225	1·27	1·77	1·65	1·56
305	1·34	1·78	1·64	1·57
400	1·40	1·79	1·65	1·56

4. Discussion

It is seen from Table II that the temperature coefficient of refractive index (dn/dt) decreases slightly with increasing wave-length. But it remains practically constant up to the highest temperature investigated here. From the dispersion formula given in the last section, the temperature coefficient of n will come out (Radhakrishnan, 1950) as

$$\frac{dn}{dt} = -\gamma_t \frac{(n^2-1)}{2n} + \frac{2b\nu_0^2 \chi_t}{2n(\nu_0^2 - \nu^2)^2}, \tag{2}$$

where γ_t, the volume coefficient of expansion, is given by $3\alpha_t$ and χ_t is the magnitude of the proportional rate of variation of ν_0 with temperature, *i.e.*,

$$\chi_t = -\frac{1}{\nu_0}\frac{d\nu_0}{dt}. \tag{3}$$

Solving for χ_t after substituting numerical values at λ 4358, λ 5461 and λ 5893, we obtain

$$\chi_t = \left\{ \begin{array}{l} 0{\cdot}264\left[\left(\frac{dn}{dt}\right)_{4358} + 1{\cdot}775\alpha\right] \\ 0{\cdot}279\left[\left(\frac{dn}{dt}\right)_{5461} + 1{\cdot}75\ \alpha\right] \\ 0{\cdot}280\left[\left(\frac{dn}{dt}\right)_{5893} + 1{\cdot}74\ \alpha\right] \end{array} \right\} \quad (4)$$

The values of χ_t at various temperatures are shown below:—

TABLE III

Temperature (deg. C.)	$10^5\chi_t$		
	4358	5461	5893
65	1·00	1·01	1·00
145	1·03	1·04	1·04
225	1·06	1·08	1·07
305	1·10	1·11	1·10
400	1·13	1·14	1·13

The constancy of the χ values at each temperature confirms the accuracy of the experiment and the correctness of the dispersion formula. As in most crystals, χ increases with temperature. The magnitude of χ is about the same as in diamond (which is also characterised by a positive dn/dt), but it is smaller than the usual value (3 to 5×10^{-5}) found in most crystals. This is probably due to the highly covalent nature of the binding of the crystal as in diamond, which results also in great hardness and high melting point. The sign of dn/dt is determined by the volume term $-\gamma(n^2-1)/2n$ and the χ term. Despite the low value of χ this sign turns out to be positive because of the low thermal expansion, and the high oscillator strength of the ultra-violet characteristic frequency. The χ term and the volume term increase at the same rate with temperature, but with opposite signs so that dn/dt is constant over the temperature range studied.

The author expresses here his thanks to Prof. R. S. Krishnan and Dr. G. N. Ramachandran under whose guidance this investigation was carried out. He specially thanks Dr. G. N. Ramachandran for having lent him a crystal of magnesia from his collection.

Summary

The temperature coefficient of refraction of magnesium oxide has been determined from room temperature to 400° C. at three wave-lengths, λ 4358, λ 5461 and λ 5893. The coefficients are found to be positive, as is to be expected from photo-elastic data. The values are discussed in the light of a dispersion formula for magnesium oxide newly proposed by the author, and are used to calculate the temperature shift of the effective characteristic frequency of the crystal in the ultra-violet.

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STUDIES IN OXYCELLULOSE

Part I. Some Properties of Accelerated Oxidation Oxycelluloses

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Nabar, Scholefield and Turner[1] have shown that the accelerated oxidation of cotton cellulose by sodium hypochlorite solutions in presence of reduced Cibanone Orange R is characterised by simple and regular relationships between the measured chemical properties of the oxycellulose formed. They attribute this simplification of the relationships to a simple mechanism of oxidation of the cellulose molecule. Their important contribution to the study of the mechanism of accelerated oxidation is the approximately constant ratio of 2 obtained between the reducing and the acidic groups formed in the products of accelerated oxidation as distinct from that obtained by the slow normal oxidation of cellulose. The conditions of oxidation such as pH of the oxidising medium, its strength and the time of treatment did not affect this ratio.

With a view to investigate if similar behaviour is exhibited by other vat dyes, the investigation was extended to a few more vat dyes including those susceptible to chemical modification or destruction by hypochlorite solutions. The chemical properties of the cellulose substrate dyed with these dyes and modified as described above[1] were examined. It was found that the chemical properties showed simple relationships amongst themselves as was the case when the behaviour of Cibanone Orange R was examined. However, only those dyes which apparently did not appear to have undergone any modification with the hypochlorite treatment showed a ratio of approximately 2 between the aldehyde and carboxyl groups formed in the oxycellulose. On the other hand, with dyes such as Ciba Blue 2 B, Caledon Jade Green XS, Indanthrene Blue R, etc., which suffered modification as a result of hypochlorite treatment, the above ratio was found to be approximately 1. From this difference in the ratio, it appears that the mode of oxidation of cellulose in the two cases is not the same. The present paper gives an account of these measurements and clearly brings out the difference in the two cases.

Experimental

Materials.—The cotton used for the experiments was 2/28's gassed supercombed fully bleached yarn. After thorough washing in hot and in cold water, the cotton had the following properties: Copper number (micro-Braidy method)[2] = 0·015, cuprammonium fluidity (0·5% solution)[3] = 3·7; milliequivalents of –COOH per 100 gm. cellulose[4] = 0·5.

The cotton was dyed with the various vat dyes by the method described in the previous communication[1] taking 2% of the solid commercial dye on weight of the cotton. The dyeing and reoxidation, washing, drying and conditioning of the dyed yarn was carried out in a dark room.

The hypochlorite solution was prepared from concentrated sodium hypochlorite, prepared according to the method of Musprat and Smith.[5] This was stored away from light. Before use, a portion of this solution was neutralised with 2 N hydrochloric acid to a pH of 7 as determined by the glass electrode. It was then diluted with the appropriate buffer solution until the available chlorine content was reduced to approximately 3 gm./l. The pH of the solution was then determined by a glass electrode with a valve potentiometer supplied by the Cambridge Scientific Instruments Co., Ltd., England.

Buffer Systems.—The pH range employed in this investigation was covered by using the following buffer systems. Mixtures[6] of M/15 Na_2HPO_4 with M/15 KH_2PO_4 for pH values 5·2 to 8. Mixtures[6] of M/5 acetic acid with M-5 sodium acetate for pH values 3 to 4·5. M/20 Borax[6] for pH 9·1. M/5 $NaHCO_3$ and M/5 Na_2CO_3[7] for pH 9 to 10.

Reduction of the Dyeing and its Hypochlorite Treatment

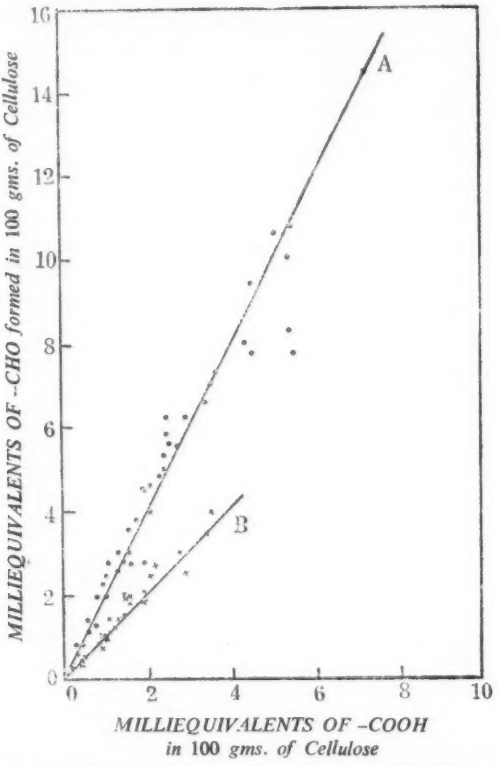
The reduction of the dyeing was carried out using 2% cold sodium hydrosulphite solution, followed by washing in air-free distilled water to remove the hydrosulphite. The reduced washed dyeing was then treated for ten minutes with buffered sodium hypochlorite solution as described in the previous communication.[1]

Determination of Copper Number

The copper number was determined by Hayes' micromethod.[2] Due to the high level of degradation, half the weight of sample normally recommended has been taken. Another noteworthy feature is that N/25 permanganate is replaced by N/25 Ceric Sulphate using *o*-ferrous-phenanthroline as indicator.

Determination of Carboxyl Content by Neale's Method[4]

One g. of the cation-free dry material is suspended in a mixture of 20 ml. of 0·02 N caustic soda (carbonate-free) and 20 ml. of 5% pure sodium chloride. At the end of one hour the excess alkali is back titrated with 0·02 N hydrochloric acid using bromo-cresol-purple indicator.



TEXT-FIG. 1. Relation between carboxylic acid groups and aldehyde groups in accelerated Oxidation Oxycelluloses

EXPERIMENTAL RESULTS AND DISCUSSION

The results of reducing and carboxyl group determination for dyes resistant to hypochlorite attack are summarised in Table I and those for dyes susceptible to modification or oxidation are summarised in Table II. These results have been represented graphically in the figure. Straight line A represents the relation between aldehyde groups and carboxyl groups for dyes which are unaffected by hypochlorite treatment. Straight line B

TABLE I

Vat Dyestuff used for the dyeing	pH of hypochlorate solution	Milliequivalents of CHO per 100 gm. of oxycellulose	Milliequivalents of COOH per gm. of oxycellulose	Ratio $\frac{CHO}{COOH}$	Mean value for ratio
Cibanone Yellow G.C.	5·6	4·5	1·9	2·37	
	6·1	6·2	2·9	2·14	
	6·5	7·7	3·6	2·14	
	7·0	9·4	4·6	2·04	
	7·3	8·0	4·4	1·82	
	8·1	4·0	2·2	1·82	
	8·7	2·7	1·9	1·42	
	9·3	1·9	1·0	1·90	1·95
Cal. Gold Orange G.	5·3	2·7	1·1	2·46	
	5·9	3·0	1·3	2·31	
	6·5	4·6	2·1	2·19	
	7·5	2·8	1·4	2·00	
	8·2	0·6	·3	2·00	
	9·0	0·4	·25	1·60	2·09
Ind. Yellow G.	6·1	4·8	2·3	2·09	
	6·5	5·8	2·5	2·32	
	7·1	6·2	2·5	2·48	
	8·0	2·6	1·3	2·00	
	8·9	0·8	0·3	2·67	2·31
Ind. Dark Blue BO.	4·2	8·3	5·5	1·51	
	4·5	10·0	5·5	1·82	
	4·6	10·7	5·6	1·91	
	5·4	14·4	7·4	1·95	
	6·1	10·6	5·2	2·04	
	6·7	3·9	2·1	1·86	
	7·0	2·7	1·7	1·59	
	8·2	1·1	0·6	1·83	
	9·0	0·2	0·1	2·00	1·83
Cal. Black B.	4·1	7·0	3·6	1·95	
	5·3	9·4	4·6	2·04	
	6·0	7·3	3·7	1·97	
	6·9	3·7	1·8	2·06	
	7·0	3·0	1·6	1·88	
	8·1	1·2	0·8	1·50	
	9·2	0·8	0·4	2·00	1·91
Cibanone Orange R.	4·99	1·92	0·76	2·53	
	5·98	5·28	0·43	2·18	
	6·06	5·60	2·63	2·14	
	7·3	6·56	3·41	1·93	
	8·07	5·54	2·68	2·06	
	8·54	3·68	1·68	2·19	
	9·06	2·40	1·05	2·29	2·19
Cib. Yellow R.	5·07	1·36	0·6	2·27	
	6·08	3·04	1·57	1·94	
	6·51	4·48	1·96	2·29	
	7·32	4·96	2·40	2·07	
	8·15	3·57	1·61	2·22	
	9·1	2·24	0·96	2·23	2·19

TABLE II

Dyestuff used for the dyeing	pH of hypochlorite solution	Milliequivalents of CHO per 100 gm. of oxycellulose	Milliequivalents of COOH per 100 gm. of oxycellulose	Ratio $\frac{COH}{COOH}$	Mean value for ratio
Indanthrene Blue RS.	5·18	1·0	0·9	1·11	
	6·05	1·9	1·5	1·27	
	7·03	2·4	2·1	1·14	
	8·10	1·4	1·1	1·27	
	9·13	0·4	0·4	1·00	1·16
Indanthrene Blue 5G	4·3	1·5	1·4	1·07	
	5·3	1·8	1·6	1·13	
	5·8	1·4	1·3	1·08	
	6·6	1·1	1·1	1·00	
	7·1	1·0	1·0	1·00	
	7·3	1·0	1·0	1·00	
	7·8	0·8	0·8	1·00	
	8·3	0·5	0·5	1·00	1·04
Ciba Blue 2B.	4·6	1·9	1·6	1·2	
	5·4	2·1	1·9	1·1	
	5·8	2·7	2·2	1·2	
	6·3	1·5	1·4	1·1	
	7·3	0·8	0·8	1·0	
	8·0	0·5	0·5	1·0	1·1
Caledon Jade Green XS.	4·1	2·8	3·0	0·93	
	4·4	3·4	3·4	1·00	
	5·1	3·9	3·6	1·08	
	6·0	2·5	2·9	0·86	
	6·1	2·0	1·7	1·18	
	6·2	1·8	1·9	0·95	
	7·5	1·2	1·2	1·00	
	8·2	0·9	0·7	1·29	
	9·1	0·4	0·3	1·33	1·07

represents similar-relationship for dyes which are modified by hypochlorite treatment.

It was considered worthwhile to attempt to calculate the amount of aldehyde groups from the copper number value for each oxidation product. Determination of the reducing power of some of the simple carbohydrates which can be obtained in pure form, have been made by a number of workers.[8] Although each reducing end group should require one atom of oxygen for its conversion to carboxyl, it has been shown experimentally that from 1 to 5 oxygen atoms may be taken up according to the choice of the oxidising agent and the conditions under which it is applied. Extension of results obtained with simple sugars such as glucose and maltose to more complex carbohydrates such as hydrocellulose, oxycellulose, etc., should be made with reserve. However, keeping in mind the limitations, if the value obtained

by Richardson, Higginbotham and Farrow[9] for maltose by the Braidy copper number method namely, that, one reducing group is equivalent approximately to 5 atoms of oxygen is made provisionally applicable to the above oxycelluloses, it is possible to calculate the actual aldehyde content. In the above tables the values of actual aldehyde groups calculated as described above are given and the results clearly show the difference between the oxidation of cellulose in the presence of non-destructible and destructible vat dyes. That the ratio $\frac{-CHO}{-COOH}$ is half in the case of the destructible dyes as compared to that for non-destructible dyes, is a strong indication of the different behaviour of the cellulose molecule in the two cases.

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SOLUTION OF GENERALIZED WAVE EQUATIONS OF ORDER HIGHER THAN 2

I

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Introduction

In a real vector space S_m of $m+1$ dimensions ($m \geq 1$) in which for any vector x from the origin to the point $x = (x^0, x^1, \ldots, x^m)$ the scalar square is defined by

$$(x \cdot x) = g_{ij} x^i x^j, \tag{1}$$

the metric tensor g_{ij} being given by

$$g_{00} = -g_{11} = \ldots = -g_{mm} = 1, \; g_{ij} = 0 \text{ for } i \neq j, \tag{2}$$

the Lorentz group $\wedge_m$ is defined as the set of all linear co-ordinate transformations which leave invariant $(x \cdot x)$ for every x in S_m. Unless explicitly indicated otherwise, a summation from 0 to m is understood over every Latin index occurring both above and below as in (1). The contravariant components x_i of the vector x are as usual defined in terms of its covariant components x^i by

$$x_i = g_{ij} x^j. \qquad (i = 0, 1, \ldots, m) \tag{3}$$

The differential operators

$$\partial_i = \frac{\partial}{\partial x^i}$$

$$\text{and } \partial^i = \frac{\partial}{\partial x_i} \qquad (i = 0, 1, \ldots, m) \tag{4}$$

transform like a contravariant and covariant vector respectively in S_m. It, therefore, follows from a well-known theorem (Weyl, 1946, Ch. II) that any invariant operator (*i.e.*, invariant with respect to $\wedge_m$) which is a rational integral function of the ∂_i's and ∂^i's is a polynomial in the only invariant of degree 2, namely the d'Alembertian

$$\Box = \partial_i \partial^i. \tag{5}$$

Any such polynomial can be factorized (in the field of complex numbers in which we work) into a product of linear factors, thus

$$(\Box + \chi_1^2)(\Box + \chi_2^2)\ldots.(\Box + \chi_n^2),$$

where amongst the χ's, which are complex numbers, some may be equal to each other.

The most general equation involving only invariant differential operators can, therefore, be written in the form

$$\prod_{r=1}^{n} (\Box + \chi_r^2)^{p_r} \psi = f(x) \tag{6a}$$

the p's being integers ≥ 1 and f being a given function of the co-ordinates $(x^0, x^1, \ldots, x^m)$.

The simplest of such equations, *viz.*, the second order inhomogeneous equation

$$(\Box + \chi^2)\psi = f(x)$$

and the corresponding homogeneous equation

$$(\Box + \chi^2)\psi = 0$$

are, for $m = 3$, of great importance in physics as relativistic wave equations; their solutions for this case (as also for arbitrary m) have been extensively studied by physicists and mathematicians, amongst the latter notably by Hadamard (1932), and extensively applied to physical problems.

In recent years, however, relativistic wave equations of order higher than two have also been introduced in physical theories. Thus in Bhabha's (1945, 1949 *a*) theory of elementary particles there occur equations of the form ($m = 3$)

$$(\Box + \chi_1^2)(\Box + \chi_2^2)\ldots.(\Box + \chi_n^2)\psi = 0,$$

the various (real) χ's being connected with the different mass-states in which, according to this theory, a particle with a given maximum spin is capable of appearing. Of particular importance is the case in which all the χ's are the same, *i.e.*, in which the particle has only one rest mass. Bhabha has shown (1949 *a*, lemma 10) that ψ then satisfies the wave equation ($m = 3$)

$$(\Box + \chi^2)^p \psi = f(x), \tag{6 b}$$

where p is any integer ≥ 1. The usual second order wave equation is only a particular case of this.

Podolsky (1942) also introduced a fourth order wave equation in relativistic electrodynamics in an attempt to avoid the divergence difficulties,

and recently Green (1948) has considered an eighth order equation in the theory of wave-fields.

Apart from purely mathematical curiosity, it therefore appears to be of considerable physical interest to investigate the solutions of generalized wave equations of arbitrary order of the form (6 *a*). Such an attempt was undertaken for the case $m = 3$ at the suggestion of Dr. Bhabha but it appeared very natural to extend the results to the general case of arbitrary m. In this paper are given the solutions of the inhomogeneous equation (6 *a*) with a right-hand member which is an arbitrary summable function.

§1. *Notation*

With every vector A of S_m having the time component A° and space components $A^1, A^2, \ldots, A^m$, for which the length $|A|$ is defined by

$$|A|^2 = (A \cdot A) = (A_i A^i) \tag{7}$$

with the convention that $|A|$ is to be taken positive when $|A|^2 > 0$, may be associated a *space vector* (denoted by the corresponding letter in heavy type) **A** whose covariant (contravariant) components are the m covariant (contravariant) space components of A and for which the length is defined by

$$\hat{A} = +\left(-\sum_{i=1}^{m} A_i A^i\right)^{\frac{1}{2}}. \tag{8}$$

Then we have the relation

$$|A|^2 = (A^\circ)^2 - \hat{A}^2. \tag{9}$$

It is convenient to consider three different cases for the equation (6 *a*) according as the differential operator has

(i) only non-repeated factors,

(ii) a single repeated factor,

or (iii) several repeated factors.

We accordingly introduce the following notations:

$$\left.\begin{aligned} \angle^n &= \overset{*}{\Pi}_{r=1} (\Box + \chi_r^2), \qquad \chi_r \neq \chi_s \text{ for } r \neq s, \\ \mathrm{L}^{(p)} &= (\Box + \chi^2)^p, \\ \mathrm{L}^{(p_1, p_2, \ldots p_n)} &= \overset{*}{\Pi}_{r=1} (\Box + \chi_r^2)^{p_r}, \qquad \chi_r \neq \chi_s \text{ for } r \neq s. \end{aligned}\right\} \tag{10}$$

When necessary an explicit dependence on m will be indicated by writing the value of m as a subscript on the right, *e.g.*, $\Box_3$. For the purpose of this paper the χ's are to be taken as real constants and $m > 1$.

§2. *Generalized wave equation with non-repeated factors*

We now proceed to consider the inhomogeneous equation

$$\angle^n \psi = f, \tag{11}$$

$f = f(x)$ being a given function of the co-ordinates $(x^0, x^1, \ldots, x^m)$ which is summable everywhere.

Following Bhabha (1939) we shall obtain a particular solution of (11) by the use of the general (though not perfectly rigorous*) method of Fourier integrals.

We assume that $f(x)$ and $\psi(x)$ are such that their Fourier transforms $\bar{f}(k)$ and $\bar{\psi}(k)$ exist in the k-vector space, where $k = (k_0, k_1, \ldots, k_m)$, so that we can write

$$\left.\begin{aligned} f(x) &= \frac{1}{(2\pi)^{\frac{m+1}{2}}} \int d\mathbf{k}\, dk_0\, \bar{f}(k)\, e^{\iota k_j x^j}, \\ \psi(x) &= \frac{1}{(2\pi)^{\frac{m+1}{2}}} \int d\mathbf{k}\, dk_0\, \bar{\psi}(k)\, e^{\iota k_j x^j}, \end{aligned}\right\} \quad (\iota^2 = -1) \tag{12}$$

It is convenient to use, as above, the abbreviations $d\mathbf{k} = dk_1 dk_2 \ldots dk_m$ and $d\mathbf{x} = dx^1 dx^2 \ldots dx^m$ for the m-dimensional volume elements and to put a single integral sign even for a multiple integral. The limits of integration, unless explicitly indicated, are to be understood to be from $-\infty$ to $+\infty$ for each variable. Further, the same general notations as before also apply for the k-space.

On substituting the integrals in (11) the equation is seen to be satisfied if

$$\begin{aligned} \bar{\psi}(k) &= \frac{\bar{f}(k)}{\prod_{r=1}^{n} (-k_i k^i + \chi_r^2)} \\ &= \frac{\bar{f}(k)}{\prod_{r=1}^{n} (-k_0^2 + \mathrm{K}_r^2)}, \end{aligned}$$

where $$\mathrm{K}_r = +(\hat{k}^2 + \chi_r^2)^{\frac{1}{2}}. \tag{13}$$

Substituting for $\bar{\psi}(k)$ in terms of $\bar{f}(k)$ in the integral for $\psi(x)$ and then inverting the integral for $f(x)$ one obtains

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* Since this work was completed I have been informed by Dr. Bhabha that the procedure can be made rigorous by using the theory of distributions recently developed by Laurent Schwartz.

$$\psi(x) = \frac{1}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0 \frac{e^{\iota k_j x^j}}{\prod_{r=1}^{n} (-k_0^2 + K_r^2)} \int dx' dx'^0 e^{-\iota k_j x'^j} f(x'). \tag{14}$$

Assuming the possibility of interchange of the order of integration in (14) the solution can be expressed in the form

$$\psi(x) = \int dx'\, dx'^0 f(x')\, G^n(x - x'), \tag{15}$$

the function G^n being defined by

$$G^n(u) = \frac{1}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0 \frac{e^{\iota k_j u^j}}{\prod_{r=1}^{n} (-k_0^2 + K_r^2)}. \tag{16}$$

It is easy to verify that $G^n(x - x')$ satisfies the differential equation

$$\angle^n G = \delta(x - x'), \tag{17}$$

where $\delta(u)$ represents the $(m+1)$ -dimensional Dirac delta-function defined by

$$\delta(u) = \frac{1}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{\iota k_j u^j}. \tag{18}$$

$G^n(x - x')$ is, therefore, the Green's function of the equation (11) ; to evaluate it we write it in the form

$$G^n(u) = \frac{(-)^n}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{\iota \mathbf{k}\cdot\mathbf{u}} \frac{e^{\iota k_0 u^0}}{\prod_{r=1}^{n} (k_0^2 - K_r^2)}, \tag{19}$$

where

$$u = x - x', \text{ and } \mathbf{k}\cdot\mathbf{u} = \sum_{i=1}^{m} k_i u^i. \tag{20}$$

As there are no singularities of the integrand on the real axes in the complex planes of $k_1, k_2, \ldots, k_m$ the paths of integration for these variables can be taken from $-\infty$ to $+\infty$ along the respective real axes; but in the k_0-plane, on account of the singularities on the real axis at $k_0 = \pm K_r$ $(r = 1, 2, \ldots, n)$ the path of integration Γ from $-\infty$ to $+\infty$ along the real axis must be indented at these points. For reasons which will appear later we choose the path Γ to pass *below* all the singularities (Figs. 1 and 2).

To evaluate the k_0-integral in (19) we consider two separate cases.

Case (*i*) $u^0 > 0$

Let γ denote (Fig. 1) the infinite semi-circle in the upper-half of the plane with centre at the origin. Then $\gamma + \Gamma$ forms a closed contour equivalent to Γ, since the integral over γ vanishes by Jordan's lemma. Cauchy's theorem can, therefore, be used to evaluate the integral,

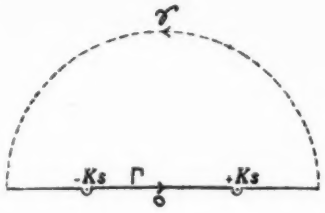

FIG. 1

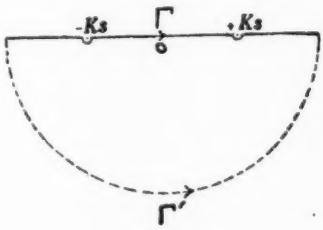

FIG. 2

The residue of the function $\dfrac{e^{ik_0u^0}}{\prod_{r=1}^{n}(k_0^2-K_r^2)}$ at $k_0=\pm K_s$ are easily seen to be

$$\pm\frac{1}{2K_s}\frac{e^{\pm iK_su^0}}{\prod_{\substack{r=1\\r\neq s}}^{n}(\chi_s^2-\chi_r^2)},$$

whence we obtain

$$G^n(u)=\frac{(-)^{n+1}}{(2\pi)^{ni}}\sum_{s=1}^{n}\frac{1}{\prod_{\substack{r=1\\r\neq s}}^{n}(\chi_s^2-\chi_r^2)}\int dk e^{ik.u}\frac{\sin(K_su^0)}{K_s}\quad(u^0>0)\cdot\qquad(21)$$

Case (ii) $u^0<0$

In this case Γ can be deformed into an infinite semi-circle Γ' below the real axis with centre at the origin (Fig. 2) and hence the k_0-integral vanishes by Jordan's lemma. Therefore

$$G^n(u)=0\qquad(u^0<0)\qquad(22)$$

The choice of Γ is now seen to be connected with the fact that it leads to a solution for G^n which vanishes on any space-like surface in the past of the point x'.

Combining (21) and (22) one obtains

$$G^n(u)=(-)^{n+1}\sum_{s=1}^{n}\frac{\bar{1}(u;\chi_s)}{\prod_{\substack{r=1\\r\neq s}}^{n}(\chi_s^2-\chi_r^2)}\qquad(23)$$

where $\bar{I}$ is defined as follows:

$$\bar{I}(u;\chi) = \begin{cases} \dfrac{1}{(2\pi)^m} \displaystyle\int dk e^{ik\cdot u} \dfrac{\sin(Ku^0)}{K} & (u^0 \geq 0) \\ 0 & (u^0 \leq 0) \end{cases} \tag{24}$$

and $$K = +(\hat{k}^2 + \chi^2)^{\frac{1}{2}}. \tag{25}$$

From formula (72) of the Appendix the value of $\bar{I}$ can be written in the form

$$\bar{I}(u;\chi) = \frac{1}{2\cdot(2\pi)^{\frac{m-1}{2}}} \left(-\frac{1}{\hat{u}}\frac{\partial}{\partial \hat{u}}\right)^l F^{\text{ret}}\left(l+1-\frac{m+1}{2}\right)(|u|;\chi), \tag{26}$$

where l is a positive integer such that

$$\frac{m}{2} > l > \frac{m-3}{2}, \tag{27}$$

and the function $F^{\text{ret}\,(q)}$ is defined by

$$F^{\text{ret}\,(q)}(|u|;\chi) = \begin{cases} \left(\dfrac{|u|}{\chi}\right)^q J_q(\chi|u|) & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}), \end{cases} \tag{28}$$

J_q being the Bessel function of the first kind of order q. (The inequalities $<$ and $>$ in (28) may be replaced by $\leq$ and $\geq$ respectively if $q > 0$.)

In particular, for *m odd* (≥ 3) we take

$$l = \frac{m-1}{2}$$

and then

$$F^{\text{ret}}\left(l+1-\frac{m+1}{2}\right)(|u|;\chi) = F_0^{\text{ret}}(|u|;\chi) \equiv \begin{cases} J_0(\chi|u|) & (u^0 \geq \hat{u}) \\ 0 & (u^0 < \hat{u}); \end{cases} \tag{29 a}$$

for *m even* (≥ 2) we take

$$l = \frac{m-2}{2}$$

and

$$F^{\text{ret}}\left(l+1-\frac{m+1}{2}\right)(|u|;\chi) = F_c^{\text{ret}}(|u|;\chi) \equiv$$

$$\begin{cases} \sqrt{\left(\dfrac{2}{\pi}\right)} \dfrac{\cos(\chi|u|)}{|u|} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{29 b}$$

We can now finally write

$$G^n(u) = \frac{(-)^{n+1}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l}\sum_{s=1}^{n}\frac{F^{\text{ret}}\left(l+1-\frac{m+1}{2}\right)(|u|;\chi_s)}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)}, \tag{30}$$

or,

$$G^n(u) = \frac{(-)^{n+1}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{\frac{m-1}{2}}\sum_{s=1}^{n}\frac{F_0^{\text{ret}}(|u|;\chi_s)}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)} \quad (m \text{ odd}) \tag{31a}$$

$$= \frac{(-)^{n+1}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{\frac{m-2}{2}}\sum_{s=1}^{n}\frac{F_\epsilon^{\text{ret}}(|u|;\chi_s)}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)} \quad (m \text{ even}). \tag{31b}$$

It may be remarked that another independent solution also exists for G^n, *viz.*, that obtained by choosing Γ to run from $-\infty$ to $+\infty$ *above* all the singularities in which case G^n vanishes on any space-like surface in the *future* of the point x'. The only difference from the previous case is that F^{ret} is replaced by another function F^{adv} obtained on replacing $\hat{u}$ by $-\hat{u}$ and reversing the inequalities in (28). These two solutions are usually referred to as the *retarded* and *advanced* solutions respectively.

It can be shown (Appendix III) that the solution given by (15) with G^n given by (31) corresponds to the initial conditions.

$$\left[\left(\frac{\partial}{\partial x^0}\right)^q\psi\right]_{x^0=0} = 0 \qquad (q = 0, 1, \ldots, 2n-1) \tag{32}$$

provided that $f(x)$ vanishes for all negative values of x^0; this is true with the possible exception of certain cases when m is even.

The form of the results for particular values of m and n can now be written down explicitly. For the case $m = 3$ we have

$$\bar{I}_3(u;\chi) = -\frac{1}{4\pi}\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}F_0^{\text{ret}}(|u|;\chi). \tag{33}$$

On carrying through the differentiation the discontinuity in F_0^{ret} at $u^0 = \hat{u}$ contributes a (one-dimensional) Dirac delta-function $\delta(u^0-\hat{u})$ so that we obtain

$$\bar{I}_3(u;\chi) = \frac{1}{4\pi}\begin{cases}\frac{1}{\hat{u}}\left[\delta(u^0-\hat{u}) - \frac{\chi\hat{u}}{|u|}J_1(\chi|u|)\right] & (u^0 \geqslant \hat{u}) \\ 0 & (u^0 < \hat{u}).\end{cases} \tag{34}$$

Since $\delta(u^0 + \hat{u})$ vanishes for $u^0 > \hat{u}$ the above can also be written as

$$I_3(u;\chi) = \frac{1}{4\pi}\begin{cases} 2\delta(|u|^2) - \dfrac{\chi}{|u|} J_1(\chi|u|) & (u^0 \geq \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{35}$$

Hence the Green's function for the case $m = 3$ is

$$G_3^n(u) = \frac{(-)^n}{4\pi}\begin{cases} 2\delta(|u|^2) \sum_{s=1}^{n} \dfrac{1}{\prod_{\substack{r=1 \\ r\neq s}}^{n} (\chi_s^2 - \chi_r^2)} - \dfrac{1}{|u|} \sum_{s=1}^{n} \dfrac{\chi_s J_1(\chi_s|u|)}{\prod_{\substack{r=1 \\ r\neq s}}^{n} (\chi_s^2 - \chi_r^2)} & (u^0 \geq \hat{u}) \\ 0 & (u_0 < \hat{u}). \end{cases} \tag{36}$$

For $n = 1$ the above reduces to

$$G_3^1(u) = \frac{1}{4\pi}\begin{cases} 2\delta(|u|^2) - \dfrac{\chi}{|u|} J_1(\chi|u|) & (u^0 \geq \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{37}$$

a result first given by Bhabha (1939).

If $n > 1$, the coefficient of the δ-term in (36) is easily seen to vanish and we obtain

$$G_3^n(u) = \frac{(-)^n}{4\pi|u|}\begin{cases} \sum_{s=1}^{n} \dfrac{\chi_s J_1(\chi_s|u|)}{\prod_{\substack{r=1 \\ r\neq 1}}^{n} (\chi_s^2 - \chi_r^2)} & (u^0 \geq \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \quad (n > 1) \tag{38}$$

We note here the remarkable feature that for the case $m = 3$ of equation (11), *the solutions obtained above are free from the δ-type singularities on the light cone when $n > 1$.* The same can be shown to be true for all equations of the form (6 *a*) of order greater than 2, that is even when several of the χ's are equal.

In general, for any odd m, the solutions of equation (11) will be free from δ-terms provided $\frac{m+1}{2} \leq n$ [see Appendix Eq. (79)].

§ 3. *Equation with a single repeated factor*

We next consider an equation of the form

$$L^{(p)}\psi = f \tag{39}$$

p being a positive integer > 1.

Proceeding exactly as in the last section the solution can be put in the form

$$\psi(x) = \int d\mathbf{x}'\, dx'^{0}\, f(x')\, G^{(p)}(x - x') \tag{40}$$

with

$$G^{(p)}(u) = \frac{(-)^p}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{i\mathbf{k}\cdot\mathbf{u}}\, \frac{e^{ik_0 u^0}}{(k_0^2 - \mathrm{K}^2)^p}. \tag{41}$$

With the same paths for integration as before, $G^{(p)}$ again vanishes for $u^0 < 0$. To evaluate it for $u^0 > 0$ we observe that (41) can be put in the form

$$G^{(p)}(u) = \frac{(-)^p}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{i\mathbf{k}\cdot\mathbf{u}}\, \frac{1}{(p-1)!} \left(\frac{\partial}{\partial X^2}\right)^{p-1} \left\{\frac{e^{ik_0 u^0}}{k_0^2 - \mathrm{K}^2}\right\},$$

which, using the result of the last section, is equal to

$$\frac{(-)^{p+1}}{(2\pi)^m} \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{u}}\, \frac{1}{(p-1)!} \left(\frac{\partial}{\partial X^2}\right)^{p-1} \left\{\frac{\sin(\mathrm{K}u^0)}{\mathrm{K}}\right\}.$$

The Green's function for this case can, therefore, be written as

$$G^{(p)}(u) = \frac{(-)^{p+1}}{(p-1)!}\, \mathrm{I}^{(p-1)}(u; \chi), \tag{42}$$

where

$$\mathrm{I}^{(\lambda)}(u; \chi) = \begin{cases} \dfrac{1}{(2\pi)^m} \displaystyle\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{u}} \left(\frac{\partial}{\partial X^2}\right)^{\lambda} \left\{\frac{\sin(\mathrm{K}u^0)}{\mathrm{K}}\right\} & (u^0 > 0) \\ 0 & (u^0 < 0). \end{cases} \tag{43}$$

Making use of the result (68) (Appendix), one finally obtains

$$G^{(p)}(u) = \frac{1}{(p-1)!\, 2^p} \frac{1}{(2\pi)^{\frac{m-1}{2}}} \left(-\frac{1}{\hat{u}} \frac{\partial}{\partial \hat{u}}\right)^{l_p} \mathrm{F}^{\mathrm{ret}\left(l_p + p - \frac{m-1}{2}\right)}(|u|; \chi), \tag{44}$$

where l_p is a positive integer satisfying the inequalities

$$\frac{m}{2} > l_p > \frac{m-1}{2} - p, \tag{45}$$

and $\mathrm{F}^{\mathrm{ret}(q)}$ is defined by (28). It is convenient to take $l_p = \dfrac{m-1}{2}$ for m odd, and $l_p = \dfrac{m-2}{2}$ for m even.

For the particular case $m = 3$ we can take $l_p = 1$ for all p so that we get

$$G_3^{(p)}(u) = -\frac{1}{2\pi} \frac{1}{(p-1)!\, 2^p} \left(\frac{1}{\hat{u}} \frac{\partial}{\partial \hat{u}}\right) \mathrm{F}^{\mathrm{ret}(p-1)}(|u|; \chi). \tag{46}$$

The absence of the δ-type singularities in the solutions of the equation of the form (39) for the case $m = 3$ and $p > 1$ is again to be noted.

It would appear that $G^{(p)}$ of (44) should be deducible from G^{p} of (30) simply by permitting the different χ's in the summation in (30) to coalesce. In doing this, however, the l's must be so chosen that $l_p = l_1$; this can be achieved, for example, by choosing the l in (27) or (45) to be the greatest positive integer satisfying the inequality $\frac{m}{2} > l$. An elegant deduction of $G^{(p)}$ from G^{p} in this way has been given by Bhabha (1949 *b*) for the case $m = 3$.

§4. *The case of repeated factors in the equation*

We finally consider the most general case in which our equation is of the form

$$L^{(p_1 p_2 \cdots p_n)} \psi = f, \tag{47}$$

where the p's are integers ≥ 1.

The solution can again be exhibited in the form

$$\psi(x) = \int d\mathbf{x}'\, dx'^0\, f(x')\, G^{(p_1, p_2, \ldots, p_n)}(x - x'), \tag{48}$$

the Green's function $G^{(p_1, p_2, \ldots, p_n)}(u)$ now being given by

$$G^{(p_1, p_2, \ldots, p_n)}(u) = \frac{(-)^{p}}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{i\mathbf{k}\cdot\mathbf{u}} \frac{e^{ik_0 u^0}}{\prod_{r=1}^{n} (k_0^2 - K_r^2)^{p_r}}, \tag{49}$$

where

$$p = \sum_{r=1}^{n} p_r. \tag{50}$$

With the usual choice for the paths of integration, the integral in (49) again vanishes for $u^0 < 0$. To evaluate $G^{(p_1, p_2, \ldots, p_n)}(u)$ for $u^0 > 0$ we first write the right-hand side of (49) as

$$\frac{(-)^{p}}{(2\pi)^{m+1}} \int d\mathbf{k}\, dk_0\, e^{i\mathbf{k}\cdot\mathbf{u}} \prod_{r=1}^{n} \frac{1}{(p_r - 1)!} \left(\frac{\partial}{\partial \chi_r^2}\right)^{p_r - 1} \left\{\frac{e^{ik_0 u^0}}{(k_0^2 - K_r^2)}\right\},$$

and then using the residues at the simple poles $k_0 = \pm K_s\ (s = 1, 2, \ldots, n)$ of the function $\frac{e^{ik_0 u^0}}{\prod_{r=1}^{n} (k^2 - K^2)}$ as in § 2, express it in the form

$$\frac{(-)^{p+1}}{(2\pi)^{m}} \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{u}} \prod_{r=1}^{n} \frac{1}{(p_r - 1)!} \left(\frac{\partial}{\partial \chi_r^2}\right)^{p_r - 1} \left\{ \sum_{s=1}^{n} \frac{1}{\prod_{\substack{r=1 \\ r \neq s}}^{n} (\chi_s^2 - \chi_r^2)} \frac{\sin(K_s u^0)}{K_s} \right\}$$

which is

$$= \frac{(-)^{p+1}}{(2\pi)^{m}} \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{u}} \sum_{s=1}^{n} \frac{1}{(p_s - 1)!} \left(\frac{\partial}{\partial \chi_s^2}\right)^{p_s - 1} \left\{ \frac{1}{\prod_{\substack{r=1 \\ r \neq 1}}^{n} (\chi_s^2 - \chi_r^2)^{p_r}} \frac{\sin(K_s u^0)}{K_s} \right\}.$$

Applying the Leibnitz theorem, the above can be written as

$$\frac{(-)^{\hat{p}+1}}{(2\pi)^m}\sum_{s=1}^{n}\sum_{\lambda=0}^{p_s-1}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot u}\frac{\binom{p_s-1}{\lambda}}{(p_s-1)!}\left(\frac{\partial}{\partial\chi_s}^2\right)^{p_s-1-\lambda}\times$$
$$\left\{\frac{1}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)^{\hat{p}_r}}\right\}\left(\frac{\partial}{\partial X_s}^2\right)^{\lambda}\left\{\frac{\sin(K_s u^0)}{K_s}\right\},$$

where the notation $\binom{p}{q}$ denotes, as usual, the binomial coefficients. Hence we can write

$$G^{(\hat{p}_1,\hat{p}_2,\ldots,\hat{p}_n)}(u)=(-)^{\hat{p}+1}\sum_{s=0}^{n}\sum_{\lambda=0}^{p_s-1}\frac{1}{\lambda!\,(p_s-1-\lambda)!}\left(\frac{\partial}{\partial X_s}^2\right)^{p_s-\lambda-1}\times$$
$$\left\{\frac{1}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)^{\hat{p}_r}}\right\}\bar{I}^{(\lambda)}(u;\chi_s) \qquad (51)$$

where $\bar{I}^{(\lambda)}(u;\chi)$ is defined by (43).

The value of $\bar{I}^{(\lambda)}$ can be written from (64) and (68) (Appendix). In this way one finally obtains

$$G^{(\hat{p}_1,\hat{p}_2,\ldots,\hat{p}_n)}(u)=\frac{(-)^{\hat{p}+1}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\sum_{s=1}^{n}\sum_{\lambda=0}^{p_s-1}\frac{(-)^{\lambda}}{2^{\lambda}\,\lambda!\,(p_s-1-\lambda)!}\left(\frac{\partial}{\partial X_s}^2\right)^{p_s-1-\lambda}$$
$$\left\{\frac{1}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)^{\hat{p}_r}}\right\}\times\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l_\lambda}\mathrm{F}^{\mathrm{ret}}\left(\lambda+l_\lambda+1-\frac{m+1}{2}\right)(|u|;\chi_s) \qquad (52\,a)$$

where the l_λ's are any positive integers satisfying the inequalities

$$\frac{m}{2}>l_\lambda>\frac{m-3}{2}-\lambda. \qquad (52\,b)$$

It is convenient to take $l_\lambda=\frac{m-1}{2}$ or $\frac{m-2}{2}$ according as m is odd or even. With this choice (52) reduces to

$$G^{(\hat{p}_1,\hat{p}_2,\ldots,\hat{p}_n)}(u)=\frac{(-)^{\hat{p}+1}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\sum_{s=1}^{n}\sum_{\lambda=0}^{p_s-1}\frac{(-)^{\lambda}}{2^{\lambda}\,\lambda!\,(p_s-1-\lambda)!}\left(\frac{\partial}{\partial X_s}^2\right)^{p_s-1-\lambda}$$
$$\left\{\frac{1}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)^{\hat{p}_r}}\right\}\times\begin{cases}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{\frac{m-1}{2}}\mathrm{F}^{\mathrm{ret}\,(\lambda)}(|u|;\chi_s) & (m\text{ odd})\\ \left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{\frac{m-2}{2}}\mathrm{F}^{\mathrm{ret}\,(\lambda-\frac{1}{2})}(|u|;\chi_s) & (m\text{ even})\end{cases} \qquad (53)$$

I wish to express my thanks to Dr. H. J. Bhabha for suggesting the problem and for his continued interest in this work. Thanks are also due to Prof. D. D. Kosambi and Dr. P. R. Masani for useful suggestions in the preparation of this paper.

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APPENDIX

I. Some results from the theory of Bessel functions

We collect here some properties of Bessel functions which are used in this paper. For more details reference may be made to Watson (1944). Here ν, μ denote unrestricted numbers while n, m denote integers; z is a complex variable.

The Bessel functions of the first kind of order ν denoted by $J_\nu(z)$ and defined by

$$J_\nu(z) = (\tfrac{1}{2}z)^\nu \sum_{r=0}^{\infty} \frac{(-)^r (\tfrac{1}{2}z)^2}{r!\,\Gamma(\nu + r + 1)}, \tag{54}$$

have the following properties:

$$J_\nu(z) = \frac{(\tfrac{1}{2}z)^\nu}{\Gamma(\tfrac{1}{2})\,\Gamma(\nu + \tfrac{1}{2})} \int_{-1}^{+1} dt\, e^{\pm izt} (1 - t^2)^{\nu - \frac{1}{2}}, \tag{55}$$

provided that $R(\nu) > -\tfrac{1}{2}$. (Poisson's integral).

$$\left(-\frac{\partial}{\partial z^2}\right)^m \left[\frac{J_\nu(az)}{z^\nu}\right] = \frac{1}{2^m}\left(-\frac{\partial}{z\partial z}\right)^m \left[\frac{J_\nu(az)}{z^\nu}\right] = \left(\frac{a}{2}\right)^m \frac{J_{\nu+m}(az)}{z^{\nu+m}}, \tag{56}$$

where $m \geq 0$ and a is a constant.

$$J_0(0) = 1,\ J_\nu(0) = 0 \text{ for } \nu > 0. \tag{57}$$

$$\lim_{z\to 0} \frac{J_\nu(az)}{z^\nu} = \frac{a^\nu}{2^\nu\,\Gamma(\nu + 1)} \tag{58}$$

$$J_{-\frac{1}{2}}(z) = \sqrt{\frac{2}{\pi z}}\cos z, \qquad J_{\frac{1}{2}}(z) = \sqrt{\frac{2}{\pi z}}\sin z \tag{59}$$

Finally, the following integral known as Sonine's discontinuous integral (Watson, 1944, p. 415), may be noted

$$\int_0^\infty J_\mu(bt)\,\frac{J_\nu\{a\sqrt{(t^2+\chi^2)}\}}{(t^2+\chi^2)^\nu}\,t^{\mu+1}\,dt = \begin{cases} \dfrac{b^\mu}{a^\nu}\left\{\dfrac{\sqrt{(a^2-b^2)}}{\chi}\right\}^{\nu-\mu-1} J_{\nu-\mu-1}\{\chi\sqrt{(a^2-b^2)}\} & (a > b) \\ 0 & (a < b) \end{cases} \tag{60}$$

Here a and b are positive and for convergence one must have $\mathrm{R}(\nu) > \mathrm{R}(\mu) > -1$; if $a = b$ then one takes $\mathrm{R}(\nu) > \mathrm{R}(\mu + 1) > 0$. χ is an unrestricted complex number.

II. *Evaluation of certain integrals*

To evaluate an integral of the form

$$\mathrm{I} = \int_{0 \leqslant k' \leqslant \hat{k} \leqslant k''} d\mathbf{k}\, g(\mathbf{k}) \tag{61}$$

(the notation being the same as in the text) where g is a given function of the variables $k_1, k_2, \ldots, k_m$ we transform to polar co-ordinates $(\hat{k}, \theta_0, \theta_1, \ldots, \theta_{m-2})$ defined as follows:

$$\begin{aligned}
k_1 &= \hat{k} \sin\theta_0 \sin\theta_1 \ldots\ldots\ldots \sin\theta_{m-2}\\
k_2 &= \hat{k} \cos\theta_0 \sin\theta_2 \ldots\ldots\ldots \sin\theta_{m-2}\\
k_3 &= \hat{k} \cos\theta_1 \sin\theta_2 \ldots\ldots\ldots \sin\theta_{m-2}\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
k_{m-1} &= \hat{k} \cos\theta_{m-3} \sin\theta_{m-2}\\
k_m &= \hat{k} \cos\theta_{m-2}.
\end{aligned}$$

The integral then can be put in the form

$$\mathrm{I} = \int_{k'}^{k''} d\hat{k}\, \hat{k}^{m-1} \int d\omega_m\, g'(\hat{k}, \theta_0, \theta_1, \ldots, \theta_{m-2}),$$

where $d\omega_m$ the element of solid angle in m dimensions, is given by

$$\begin{aligned}
d\omega_m &= \sin\theta_1 \sin^2\theta_2 \ldots\ldots \sin^{m-2}\theta_{m-2}\, d(\theta_0, \theta_1, \ldots, \theta_{m-2})\\
&= \sin^{m-2}\theta_{m-2}\, d\theta_{m-2}\, d\omega_{m-1}.
\end{aligned}$$

If, in particular, g' is a function of $\hat{k}$ and θ_{m-2} alone, then I reduces to the form

$$\mathrm{I} = \omega_{m-1} \int_{k'}^{k''} d\hat{k}\, \hat{k}^{m-1} \int_{-1}^{+1} d\xi\, (1 - \xi^2)^{\frac{m-3}{2}}\, g'(\hat{k}, \xi), \tag{62}$$

where $\xi = \cos\theta_{m-2}$ and ω_p the solid angle in p dimensions is given by

$$\omega_p = 2[\Gamma(\tfrac{1}{2})]^p / \Gamma(p/2). \tag{63}$$

We shall utilize this result to express in terms of Bessel functions of the first kind the integral

$$\mathrm{I}^{(\lambda)}(u; \chi) = \frac{1}{(2\pi)^m} \int dk\, e^{i\mathbf{k}\cdot\mathbf{u}} \left(\frac{\partial}{\partial \chi^2}\right)^{\lambda} \left\{\frac{\sin(\mathrm{K}u^0)}{\mathrm{K}}\right\}, \tag{64}$$

where $\mathrm{K} = +(\hat{k}^2 + \chi^2)^{\frac{1}{2}}$ and λ is an integer $\geqslant 0$.

For the polar variables introduced as above we choose the polar axes in such a way that the **u**-direction coincides with the co-ordinate axis with respect to which the angle θ_{m-2} is measured in the **k**-space. Then

$$\mathbf{k}\cdot u = k\hat{} u\hat{} \cos\theta_{m-2} = k\hat{}\hat{u}\xi,$$

and since the integrand in (64) depends only on $k\hat{}$ and ξ we have from (62)

$$I^{(\lambda)} = \frac{\omega_{m-1}}{(2\pi)^m}\int_0^\infty dk\hat{}\, k\hat{}^{m-1}\left(\frac{\partial}{\partial\chi^2}\right)^\lambda\left\{\frac{\sin(Ku^0)}{K}\right\}\int_{-1}^{+1} d\xi\, e^{i(k\hat{}\hat{u})\xi}(1-\xi^2)^{\frac{m-3}{2}}.$$

From (55) the R.H.S.

$$= \frac{2^{\frac{m-2}{2}}\Gamma(\frac{1}{2})\,\Gamma\left(\frac{m-1}{2}\right)\omega_{m-1}}{(2\pi)^m}\int_0^\infty dk\hat{}\, k\hat{}^{\frac{m}{2}}\left(\frac{\partial}{\partial\chi^2}\right)^\lambda\left\{\frac{\sin(Ku^0)}{K}\right\}\times \frac{J_{\frac{m-2}{2}}(k\hat{}\hat{u})}{\hat{u}^{\frac{m-2}{2}}} \tag{65}$$

provided that $R\left(\frac{m-2}{2}\right) > -\frac{1}{2}$ *i.e.*, $m > 1$.

Substituting the value of ω_m from (63) and expressing the sine functions in terms of a Bessel function from (59) we obtain

$$I^{(\lambda)} = \frac{\sqrt{u^0}}{2\cdot(2\pi)^{\frac{m-1}{2}}}\int_0^\infty dk\hat{}\, k\hat{}^{\frac{m}{2}}\left(\frac{\partial}{\partial\chi^2}\right)^\lambda\left\{\frac{J_{\frac{1}{2}}(Ku^0)}{K^{\frac{1}{2}}}\right\}\frac{J_{\frac{m-2}{2}}(k\hat{}\hat{u})}{\hat{u}^{\frac{m-2}{2}}}$$

$$= \frac{(-)^\lambda (u^0)^{\lambda+\frac{1}{2}}}{2^{\lambda+1}(2\pi)^{\frac{m-1}{2}}}\int_0^\infty dk\hat{}\, k\hat{}^{\frac{m}{2}}\frac{J_{\lambda+\frac{1}{2}}(Ku^0)\,J_{\frac{m-2}{2}}(k\hat{}\hat{u})}{K^{\lambda+\frac{1}{2}}\;\;\hat{u}^{\frac{m-2}{2}}}. \tag{66}$$

The integral on the R.H.S. of (66) is a Sonine integral which, however, is in general divergent. To deal with it we take recourse to an artifice. We introduce a parameter l (which takes non-negative integral values only) through the relation

$$\frac{J_{\frac{m-2}{2}}(k\hat{}\hat{u})}{\hat{u}^{\frac{m-2}{2}}} = \frac{1}{k\hat{}^l}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^l\left\{\frac{J_{\frac{m-2}{2}-l}(k\hat{}\hat{u})}{\hat{u}^{\frac{m-2}{2}-l}}\right\},$$

and interchange the operator $\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l}$ and the sign of integration. In this way we obtain

$$I^{(\lambda)} = \frac{(-)^{\lambda}(u^0)^{\lambda+\frac{1}{2}}}{2^{\lambda+1}\,(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l}\frac{1}{\hat{u}^{\frac{m-2}{2}-l}}\int_0^{\infty} dk\hat{}\; k\hat{}^{\frac{m}{2}-l}\,\frac{J_{\lambda+\frac{1}{2}}(Ku^0)}{K^{\lambda+\frac{1}{2}}}\,J_{\frac{m-2}{2}-l}(k\hat{}\,\hat{u}). \tag{67}$$

In order to ensure the convergence of the Sonine integral (67) we now choose $l = l_\lambda$ such that l_λ is a positive integer satisfying the inequalities

$$\lambda + \tfrac{1}{2} > \frac{m-2}{2} - l_\lambda > -1$$

i.e.,
$$\frac{m}{2} > l_\lambda > \frac{m-3}{2} - \lambda.$$

With this choice one obtains from (60), for $u^0 > 0$

$$I^{(\lambda)} = \frac{(-)^{\lambda}}{2^{\lambda+1}\,(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l_\lambda}\begin{cases}\left(\frac{|u|}{\chi}\right)^{\lambda+l_\lambda+1-\frac{m+1}{2}} J_{\lambda+l_\lambda+1-\frac{m+1}{2}}(\chi\,|\,u\,|) & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}).\end{cases}$$

When $u^0 < 0$ we apply (60) after writing $u^0 = -u'^0$ in (67) and using the fact that $u'^0 > 0$. The final result can now be written as follows:

$$I^{(\lambda)}(u;\chi) = \frac{(-)^{\lambda}}{2^{\lambda+1}\,(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l_\lambda} F^{\left(\lambda+l_\lambda+1-\frac{m+1}{2}\right)}(|\,u\,|;\chi) \tag{68}$$

where

$$F^{(q)}(|u|;\chi) = \begin{cases}\left(\frac{|u|}{\chi}\right)^{q} J_q(\chi\,|\,u\,|) & (u^0 > \hat{u}) \\ 0 & (-\hat{u} < u^0 < \hat{u}) \\ -\left(\frac{|u|}{\chi}\right)^{q} J_q(\chi\,|\,u\,|) & (u^0 < -\hat{u}),\end{cases} \tag{69}$$

and l_λ is a positive integer such that

$$\frac{m}{2} > l_\lambda > \frac{m-3}{2} - \lambda. \tag{70}$$

Some particular cases may be noted. For $\lambda = 0$ the integral $I^{(\lambda)}$ reduces to

$$I(u;\chi) = \frac{1}{(2\pi)^m}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{u}}\,\frac{\sin(Ku^0)}{K}. \tag{71}$$

From (68) we have, therefore,

$$I(u;\chi) = \frac{1}{2\cdot(2\pi)^{\frac{m-1}{2}}}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l} F^{\left(l+1-\frac{m+1}{2}\right)}(|u|;\chi), \quad (72)$$

where now l is a positive integer for which

$$\frac{m}{2} > l > \frac{m-3}{2}. \quad (73)$$

When m is odd (≥ 3), $l = \frac{m-1}{2}$ and in this case

$$F^{\left(l+1-\frac{m+1}{2}\right)}(|u|;\chi) = F_0(|u|);\chi) \equiv \begin{cases} J_0(\chi\,|\,u\,|) & (u^0 > \hat{u}) \\ 0 & (-\hat{u} < u^0 < \hat{u}) \\ -J_0(\chi\,|\,u\,|) & (u^0 < -\hat{u}); \end{cases} \quad (74)$$

while for m even (≥ 2), $l = \frac{m-2}{2}$ and

$$F^{\left(l+1-\frac{m+1}{2}\right)}(|u|;\chi) = F_e(|u|);\chi) \equiv$$

$$\begin{cases} \sqrt{\left(\frac{\chi}{|u|}\right)}J_{-\frac{1}{2}}(\chi\,|\,u\,|) = \sqrt{\left(\frac{2}{\pi}\right)}\frac{\cos(\chi\,|\,u\,|)}{|u|} & (u^0 > \hat{u}) \\ 0 & (-\hat{u} < u^0 < \hat{u}) \\ -\sqrt{\left(\frac{\chi}{|u|}\right)}J_{-\frac{1}{2}}(\chi\,|\,u\,|) = -\sqrt{\left(\frac{2}{\pi}\right)}\frac{\cos(\chi\,|\,u\,|)}{|u|} & (u^0 < -\hat{u}). \end{cases} \quad (75)$$

Finally it may be remarked that the passage from (66) to (67) is essentially the subtraction of an infinite term. This subtraction is equivalent to that involved in Hadamard's (1932, p. 184) definition of "partie finie" of an infinite integral and in Riesz's (1948) method of "analytic continuation".

III. *Initial value conditions for the solutions of generalised wave equations.**

The Green's function (30) can be written as

$$G^{n}(u) = \text{const.}\left(-\frac{1}{\hat{u}}\frac{\partial}{\partial\hat{u}}\right)^{l}\sum_{s=1}^{n}\frac{1}{\prod_{\substack{r=1\\ r\neq s}}^{n}(\chi_s^2-\chi_r^2)}\times$$

$$\begin{cases} (|u|^2)^{l+1-\frac{m+1}{2}}\sum_{t=0}^{\infty}\frac{(-)^t\,(\frac{1}{4}|u|^2\chi_s^2)^t}{t!\,\Gamma\left(t+l+2-\frac{m+1}{2}\right)} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}) \end{cases} \quad (76)$$

* I am indebted to Dr. Bhabha for the arguments of this section.

From the properties of the determinant

$$\begin{vmatrix} 1 & 1 & \cdot & \cdot & \cdot & 1 \\ \chi_1^2 & \chi_2^2 & \cdot & \cdot & \cdot & \chi_n^2 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \chi_1^{2n-2} & \chi_2^{2n-2} & \cdot & \cdot & \cdot & \chi_n^{2n-2} \end{vmatrix} \tag{77}$$

it follows that (see *e.g.*, Bhabha, 1949 *b*)

$$\sum_{s=1}^{n} \frac{(\chi_s^2)^t}{\prod_{\substack{r=1 \\ r \neq s}}^{n} (\chi_s^2 - \chi_r^2)} = \begin{cases} 0 & \text{if } t < n-1 \\ 1 & \text{if } t = n-1, \end{cases}$$

and hence

$$G^n(u) = \text{const.} \left(-\frac{1}{\hat{u}} \frac{\partial}{\partial \hat{u}}\right)^l$$

$$\begin{cases} \dfrac{(-\frac{1}{4})^{n-1} (|u|^2)^{l+n-\frac{m+1}{2}}}{(n-1)!\, \Gamma\left(l+n+1-\dfrac{m+1}{2}\right)} + \displaystyle\sum_{s=1}^{n} \sum_{t=n}^{\infty} \frac{(-)^t (|u|^2)^{l+1-\frac{m+1}{2}} (\frac{1}{4} |u|^2 \chi_s^2)^t}{\prod_{\substack{r=1 \\ r \neq s}}^{n} (\chi_s^2 - \chi_r^2)\, t!\, \Gamma\left(t+l+2-\dfrac{m+1}{2}\right)} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{78}$$

If $n > \dfrac{m+1}{2}$ the differentiations in G^n do not contribute any δ-functions and we obtain simply

$$G^n(u) = \begin{cases} O\left\{(|u|^2)^{n-\frac{m+1}{2}}\right\} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{79}$$

Now in the integral

$$\psi(x) = \int d\mathbf{x}'\, dx^{0\prime}\, f(x')\, G^n(u)$$

the integration can be taken to extend only over the volume of the section of the past light cone of the point x cut off by the plane $x^0 = 0$ (Fig. 3) if $f(x)$ vanishes for $x^0 < 0$. Since $f(x)$ is bounded and

$$|u|^2 \leq (x^0)^2$$

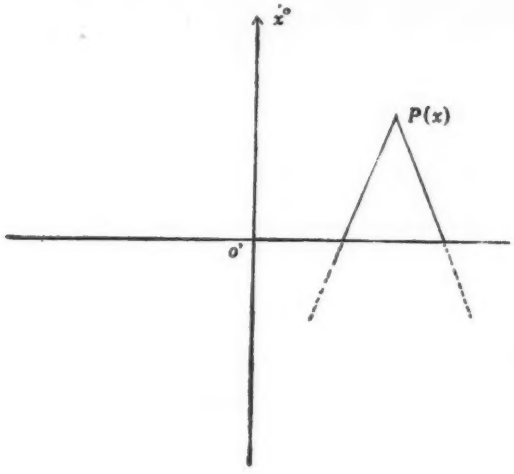

FIG. 3

throughout the volume of integration we have

$$\psi(x) \rightleftharpoons \mathrm{O}\{(x^0)^{2n-m-1}\} \int dx'\, dx^{0\prime}.$$

For small x^0 the volume is $\mathrm{O}\{(x^0)^{m+1}\}$ and hence we have

$$\psi(x) = \mathrm{O}\{(x^0)^{2n}\}, \text{ for small } x^0. \tag{80}$$

It follows, therefore, that the solution obtained in § 2 corresponds to the initial conditions

$$\left[\left(\frac{\partial}{\partial x^0}\right)^q \psi\right]_{x^0=0} = 0 \qquad (q = 0, 1, \ldots, 2n-1) \tag{81}$$

if $f(x)$ vanishes for $x^0 < 0$.

We next consider the case when $n < \dfrac{m+1}{2}$ and m is odd. Then

$$a = \frac{m+1}{2} - n$$

is an integer > 0 and $l = \dfrac{m-1}{2}$. We have therefore

$$\mathrm{G}^n(u) = \text{const.} \left(-\frac{1}{\hat{u}}\frac{\partial}{\partial \hat{u}}\right)^a \begin{cases} \mathrm{O}\{(|u|^2)^{l-a}\} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{82}$$

On differentiating $l-\alpha$ times ($l-\alpha \geq 0$ for $n \geq 1$) we obtain

$$G^n(u) = \text{const.} \left(-\frac{1}{\hat{u}}\frac{\partial}{\partial \hat{u}}\right)^{\alpha} \begin{cases} \text{const.} + O\{|u|^2\} & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}). \end{cases} \tag{83}$$

Further differentiations will contribute δ-function and its derivatives at $u^0 = \hat{u}$. The result can be written as

$$G^n(u) = \begin{cases} \sum_{\mu=1}^{\alpha} a_\mu \frac{\delta^{(\alpha-\mu)}(u^0-\hat{u})}{\hat{u}^{\mu+\alpha-1}} + \text{positive powers of } |u|^2 & (u^0 > \hat{u}) \\ 0 & (u^0 < \hat{u}) \end{cases} \tag{84}$$

where $\delta^{(\nu)}$ denotes the νth derivative of the delta function and the a_μ's are certain constants. The solution $\psi(x)$ can now be written as

$$\psi(x) = \psi_1(x) + \psi_2(x),$$

where $\psi_1(x)$ stems from the δ-terms in the Green's function and $\psi_2(x)$ from the non-singular terms in it. $\psi_2(x)$ satisfies the same initial condition as above, and it only remains to verify these for $\psi_1(x)$.

$$\begin{aligned} \psi_1(x) &= \sum_\mu a_\mu \int dx'\, dx'^0 f(x') \frac{\delta^{(\alpha-\mu)}(u^0-\hat{u})}{\hat{u}^{\mu+\alpha-1}} \\ &= \sum_\mu a_\mu \int dx' \frac{f^{(\alpha-\mu)}(x')}{\hat{u}^{\mu+\alpha-1}} \end{aligned} \tag{85}$$

where

$$f^{(\nu)}(x') = \left\{\left(\frac{\partial}{\partial x^0}\right)^{\nu} f(x')\right\}_{x^{0\prime}=x-\hat{u}}. \tag{86}$$

If all the derivatives of $f(x')$ upto order $\alpha-1$ are bounded on the surface of the past light cone then we obtain, for small x^0

$$\begin{aligned} \psi_1(x) &= O\left\{\frac{1}{(x^0)^{2\alpha-1}} \int dx'\right\} \\ &= O\{(x^0)^{m+1-2\alpha}\} \\ &= O\{(x^0)^{2n}\} \end{aligned} \tag{87}$$

whence the desired result follows. The same is easily seen to be true when $n = \frac{m+1}{2}$.

The arguments given above apply directly to the solution (40) of the equation $L^{(\rho)}\psi = f(x)$ which, therefore, also corresponds to the same initial conditions as above if $f(x)$ vanishes for $x^0 < 0$.

SUMMARY

Using the method of Fourier integrals, solutions of wave equations of the form

$$\prod_{r=1}^{n} (\Box + \chi_r^2)^{p_r} \psi = f,$$

where $\Box$ is the d'Alembertian in $m+1$ dimensions, the p's are positive integers and f is a given function of the co-ordinates, are obtained for arbirary m and n. The solutions for the two cases, *viz.*, when all the χ's are different $(p_1 = p_2 \ldots = p_n = 1)$ and when all the χ's are the same $(p_1 = p,\ p_2 = p_3 \ldots = p_n = 0)$ are considered separately in greater detail.

It is shown that the usual δ-type singularities on the light cone do not appear in the solutions of the wave equations of order higher than 2 in the case of four-dimensional space-time which is of physical importance.

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THERMAL EXPANSION OF CRYSTALS

II. Magnetite and Fluorite

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1. Introduction

In Part I of this series (Sharma, 1950) which appeared in these Proceedings, measurements on the thermal expansion of sodium chlorate and sodium bromate were reported. In continuation of this work the author has now investigated the thermal expansion of two more cubic crystals, magnetite and fluorite, and the results are presented in this paper. Both these crystals occur as natural minerals and are known since long. The properties of magnetite are peculiar in many ways. It possesses a Curie-point at about 575° C, below which it is ferromagnetic and above the Curie-point it exhibits para-magnetism. Attempts have been made to detect discontinuity in other physical properties at the Curie-point. Thus, Weiss and Beck (1908) observed an anomaly in the specific heat curve and Chevenard (1921) a similar one in the thermal dilatation. Allen (1909) detected a thermal effect accompanying the magnetic transformation and Konigsberg and Shilling (1912) observed a break in the thermal conductivity curve.

Fluorite derives its importance from the fact that due to the simplicity of its structure, many of the physical properties can be correlated with its internal constitution. Studies on the magneto-optic anomaly in fluorite by Ramaseshan (1947) in this laboratory reveal that its structure is not wholly ionic, as hitherto supposed, but partly covalent. Press (1950) has studied the temperature effect on the Raman spectrum of this crystal.

2. Previous Work

Kopp (1852) first measured the coefficient of cubical expansion of magnetite upto 50°C while Pfaff (1858) measured the linear expansion in the range 0°-100°C. The first accurate determination of thermal expansion, however, was undertaken by Fizeau (1868) by employing the phenomenon of interference of light. Chaudron and Forrestier (1924) reported in a short note that there was a continuous increase in the expansion of magnetite upto the Curie-point, thereafter there was a decrease. Further, at about 695°C the expansion curve according to them showed a kink which they

attributed to the magnetic transformations as observed by Weiss and Foex (1911). Later Forrestier (1928) working with the sesquioxide of iron prepared in the laboratory, reported a similar behaviour in the thermal dilatation. Chevenard (1921), on the contrary, had found that the change in the Curie's constant in this temperature region was not accompanied by a corresponding variation in the thermal expansion. It may be remarked that all these investigators who employed a differential dilatometer for their study, have only quoted the results of their experimental study and no specific values for either the relative changes in length, volume or the coefficient of thermal expansion are reported for the temperature interval studied by them. Only experimental curves are reproduced in their papers, which are, however, drawn in such a manner that they cannot be employed for any kind of interpolation. In view of the lack of numerical data and the conflicting opinion expressed in the literature regarding the thermal behaviour of magnetite after the Curie-point, it was considered desirable to make an accurate study of the linear expansion of this crystal over a wide range of temperature.

The first study of the thermal expansion of fluorite above the room temperature was undertaken in this laboratory by Press (1949) who has summarised in his paper the work of the previous investigators below the room temperature. He, however, studied the thermal expansion up to 260° C, as the interferometer plates used by him were of crystal quartz. With the aid of fused quartz interferometer used by the author, it has been possible to repeat the measurements on thermal expansion above the room temperature and also to extend them up to 650° C.

3. Preparation of Specimens and Experimental Technique

Magnetite crystallises in the holohedral cubic system; but cubic crystals are rare. The habit is more commonly octahedral or dodecahedral with the faces striated parallel to the (110):(111) — edge. The crystals used for the present study were of iron-black colour and had their dodecahedral faces fully developed. A preliminary determination of the specific gravity of all the samples in collaboration with Rao, who (1950) determined the elastic constants for this crystal by ultrasonic method, revealed the existence of crystals having different densities. Three crystals of exactly equal density (5·180 gm/cc) were selected from the lot and their lower pyrimidal form was ground and polished flat, thus resulting in a right pyramid standing on a practically square base and tapering to a natural apex at the top. The heights of the specimens were adjusted to the same value with the help of the micrometer screw. During the actual run of the experiment

it was in fact found that the configuration and the orientation of the interference pattern did not appreciably change even without a spacer being weighted. This was firstly due to the stability of the spacers, as well as due to an exceedingly pointed apex which did not have much contact surface with the upper interferometer plate, thus considerably reducing the possibility of formation of varying thicknesses of the air film in between the two.

The fluorite crystal used was a clear, transparent and colourless piece in the form of a triangular prism. Three pieces were cut parallel to the natural cleavage plane and turned into the required pyramidal shape as usual.

The further details of the experimental technique are already described in paper I of this series.

4. Observation Data and Results

With magnetite the whole run of the experiment was divided in two steps. In the first run the study was confined upto about 500° C and the relative changes of length with temperature are entered in Table I and the

Table I. *Relative changes of length for magnetite*

$L_0 = 0{\cdot}4435$ cm.
$\lambda_v = 5462{\cdot}2$ Å. Barometric height = 687 mm.
$\frac{\lambda_v}{2L_0} = 0{\cdot}0_461581$

(I Run)

No. of fringes (ΔN)	Temperature (° C.)	$\frac{\lambda_v}{2L_0}\ \Delta N \times 10^8$	Air correction $\times 10^6$	$\frac{\Delta L}{L_0} \times 10^8$
0	29·7	..	..	..
3	52·9	0·18474	17·1	0·20184
6	75·4	0·36948	31·4	0·40088
9	97·1	0·55423	43·5	0·59773
12	118·2	0·73897	54·0	0·79297
15	138·4	0·92371	63·1	0·98681
18	157·8	1·1085	71·0	1·1795
21	176·8	1·2932	78·1	1·3713
24	195·4	1·4779	84·5	1·5624
28	218·4	1·7243	91·7	1·8160
32	240·9	1·9706	98·1	2·0687
36	261·8	2·2169	103·6	2·3205
40	281·8	2·4632	108·4	2·5716
44	301·0	2·7095	112·8	2·8223
48	319·4	2·9559	116·7	3·0726
52	336·9	3·2022	120·1	3·3223
56	353·5	3·4485	123·3	3·5718
60	369·8	3·6948	126·3	3·8211
65	388·8	4·0027	129·5	4·1322
70	407·6	4·3106	132·5	4·4432
75	426·0	4·6185	135·3	4·7538
80	443·4	4·9264	137·8	5·0642
85	459·8	5·2344	140·1	5·3745
90	475·6	5·5423	142·1	5·6844
95	491·2	5·8502	144·1	5·9943

TABLE II. *Relative changes of length for magnetite*

(II Run)

$\frac{\lambda_D}{2L_0} = 0{\cdot}0_461581$ Barometric height = 685 mm.

No. of fringes (ΔN)	Temperature (° C.)	$\frac{\lambda_D}{2L_0}\Delta N \times 10^3$	Air correction $\times 10^6$	$\frac{\Delta L}{L_0} \times 10^3$
0	461·6	..	..	..
8	486·7	0·4926	3·25	0·4959
16	510·8	0·9853	6·17	0·9915
24	533·5	1·4779	8·76	1·4867
32	555·4	1·9706	11·1	1·9817
36	565·8	2·2169	11·9	2·2288
40	577·3	2·4632	13·4	2·4766
44	588·6	2·7095	14·5	2·7240
50	604·9	3·0790	16·0	3·0950
60	630·8	3·6948	18·4	3·7132
70	655·5	4·3106	20·5	4·3311
80	678·6	4·9264	22·4	4·9488
85	689·9	5·2344	23·3	5·2577
90	701·1	5·5423	24·2	5·5665
95	711·9	5·8502	25·0	5·8752

Note.—In computing the air correction the slight difference in the atmospheric pressure from that in the previous run has been neglected.

TABLE III. *Coefficient of linear expansion for magnetite*

$\alpha_t = 0{\cdot}0_58417 + 0{\cdot}0_84051\,t + 0{\cdot}0_{10}4146t^2$ (Below the Curie-pt.)

$\alpha_t = 0{\cdot}0_57674 + 0{\cdot}0_81235\,t + 0{\cdot}0_{10}4029t^2$ (Above the Curie-pt.)

Temperature (° C.)	$\alpha \times 10^6$ (Observed)	$\alpha \times 10^6$ (Calculated)	Difference (%)
41·3	8·698	8·655	+0·5
86·2	9·074	9·074	..
128·3	9·594	9·619	−0·3
167·3	10·09	10·26	−1·7
206·9	11·03	11·03	..
251·4	12·05	12·06	..
291·4	13·05	13·12	−0·5
328·2	14·29	14·21	+0·6
361·7	15·30	15·31	..
398·2	16·51	16·60	−0·4
434·7	17·84	18·01	−1·0
467·7	19·62	19·38	+1·2
483·4	19·87	20·06	−1·0
474·2	19·75	19·66	+0·5
498·8	20·56	20·75	−0·9
522·2	21·82	21·84	..
544·5	22·60	22·91	−1·4
560·6	23·76	23·72	..
Curie-point			
571·5	21·55	21·54	..
583·0	21·90	22·09	−0·9
596·8	22·76	22·76	..
617·9	23·86	23·82	..
643·2	25·01	25·13	−0·5
667·0	26·74	26·43	+1·2
684·3	27·34	27·39	..
695·5	27·57	28·02	−1·6
706·5	28·59	28·66	−0·2

TABLE IV. *Relative changes of length for fluorite*

$L_0 = 0{\cdot}2992$ cm.
$\lambda_p = 5462{\cdot}2$ Å
$\frac{\lambda_p}{2L_0} = 0{\cdot}0_4 91280$

Barometric height = 686 mm.

No. of fringes (ΔN)	Temperature (° C.)	$\frac{\lambda_p}{2L_0} \cdot \Delta N \times 10^3$	Air correction $\times 10^6$	$\frac{\Delta L}{L_0} \times 10^3$
0	28·3	..	..	..
6	57·7	0·5477	21·3	0·5690
12	86·4	1·0954	38·7	1·1341
18	114·5	1·6430	53·2	1·6962
24	141·6	2·1907	65·4	2·2561
30	167·5	2·7384	75·6	2·8140
36	192·9	3·2861	84·5	3·3706
42	217·8	3·8338	92·4	3·9262
48	242·0	4·3814	99·3	4·4807
54	265·4	4·9291	105·3	5·0344
60	288·1	5·4768	110·8	5·5876
68	317·9	6·2070	117·2	6·3242
76	346·5	6·9373	122·8	7·0601
84	374·1	7·6675	127·8	7·7953
92	400·6	8·3978	131·8	8·5296
100	426·3	9·1280	136·1	9·2641
108	451·6	9·8582	139·7	9·9979
116	476·2	10·5885	143·0	10·7315
124	499·8	11·3187	146·0	11·4647
132	522·8	12·0490	148·6	12·1976
140	545·3	12·7792	151·1	12·9303
150	572·8	13·6920	154·0	13·8460
160	599·4	14·6048	156·6	14·7614
170	624·8	15·5176	159·0	15·6766
180	649·7	16·4304	161·2	16·5916

coefficients of expansion are presented in Table III upto the thick dividing line drawn across the table. In Table II are contained the values for changes in length encountered during the course of the subsequent run of the experiment from about 460° C to 710° C and the corresponding coefficients of expansion are also entered in Table III below the separating line. The necessary data for fluorite are presented in Tables IV and V. The former table contains the relative changes of length, while the latter gives the coefficient of expansion at different temperatures. It has been found that the coefficient of expansion of each crystal can be correlated with an interpolation formula of the parabolic type. The formula for fluorite is given at the top of Table V, while two formulæ, one valid below the Curie-point and the other above it, are given for magnetite at the top of Table III. The values of thermal expansion calculated from these formulæ are entered in the third column of the appropriate table, and the difference, in per cent, between the observed and calculated values of the coefficients of expansion is presented in the last column of the same tables.

TABLE V. *Coefficient of linear expansion for fluorite*

$\alpha_t = 0{\cdot}0_4 1851 + 0{\cdot}0_7 1481\, t + 0{\cdot}0_{10} 2152\, t^2$

Temperature (° C.)	$\alpha \times 10^6$ (Observed)	$\alpha \times 10^6$ (Calculated)	Difference (%)
43·0	19·36	19·19	+0·9
72·1	19·69	19·69	..
100·5	20·00	20·22	−1·1
128·1	20·65	20·76	−0·5
154·6	21·54	21·31	+1·1
180·2	21·92	21·88	..
205·4	22·31	22·46	−0·7
229·9	22·92	23·05	−0·6
253·7	23·66	23·65	..
276·8	24·37	24·26	+0·5
303·0	24·73	24·97	−0·9
332·2	25·72	25·80	−0·3
360·3	26·64	26·64	..
387·4	27·71	27·47	+0·9
413·5	28·59	28·32	+0·9
439·0	29·00	29·16	−0·5
463·9	29·80	30·01	−0·7
488·0	31·07	30·86	+0·7
511·3	31·86	31·71	+0·5
534·1	32·56	32·56	..
559·0	33·30	33·51	−0·6
586·1	34·42	34·58	−0·5
612·1	36·03	35·64	+1·1
637·3	38·75	36·68	..

TABLE VI

Substance	Temperature (° C.)	Values of the author	Values in the literature	Authors
		$\times 10^6$	$\times 10^6$	
Fe_3O_4 ..	17–50	8·61	9·67	Kopp (1852)
	0–100	8·83	9·54	Pfaff (1858)
	40	8·65	8·46(1)	Fizeau (1888)
CaF_2 ..	5·5	18·59	18·53(2)	Valentiner and Wallot (1915)
	0–100	19·36	19·50	Pfaff (1858)
	40	19·14	19·11	Fizeau (1868)
		,,	20·94	Press (1949)
	52	19·34	19·34	Wiedman (1889)
	50	19·30	21·02	Press (1949)
	100	20·21	21·40	
	150	21·22	21·62	
	200	22·33	22·50	
	250	23·56	23·45	

Note.—(1) Reported in I.C. Tables (1928). (2) From low temperature work.

The relative changes of length for magnetite and fluorite are represented graphically in Figs. 1 and 2 respectively. Curves marked I and II

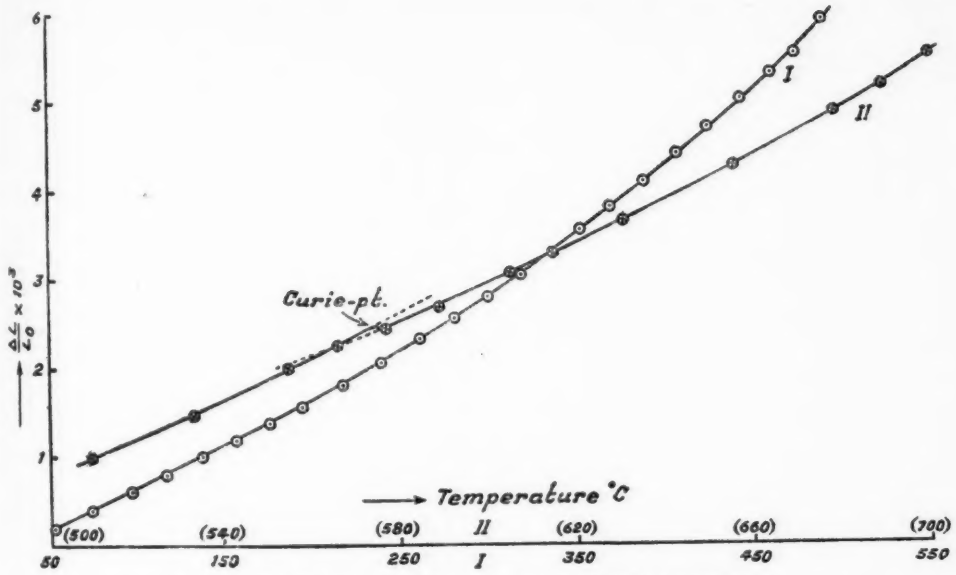

FIG. 1. Relative changes of length of magnetite with temperature.

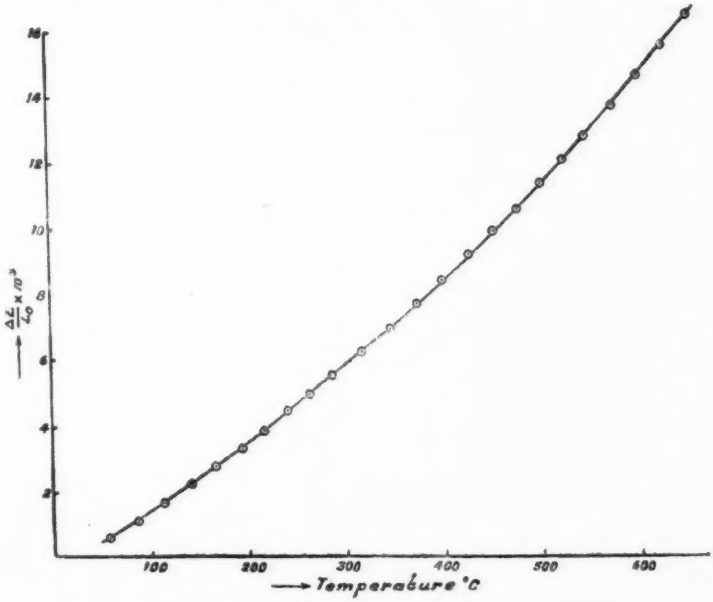

FIG. 2. Relative changes of length of fluorite with temperature.

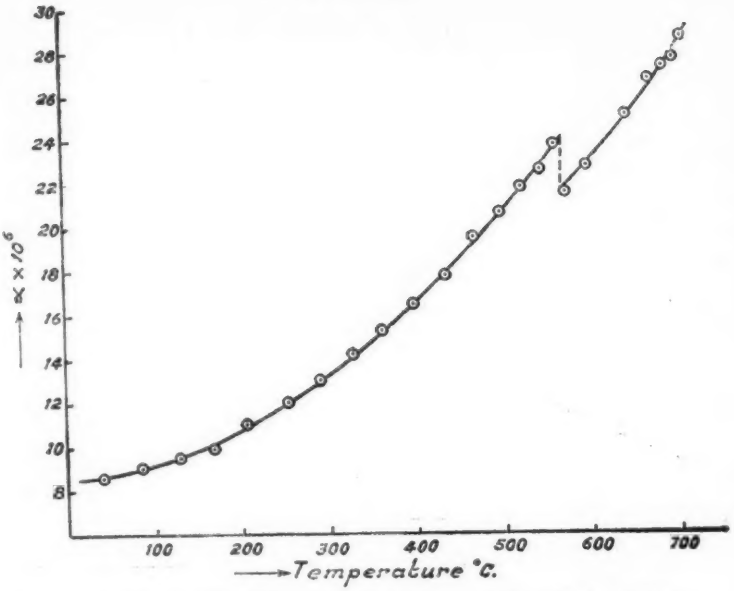

FIG. 3. Variation of coefficient of expansion of magnetite with temperature.

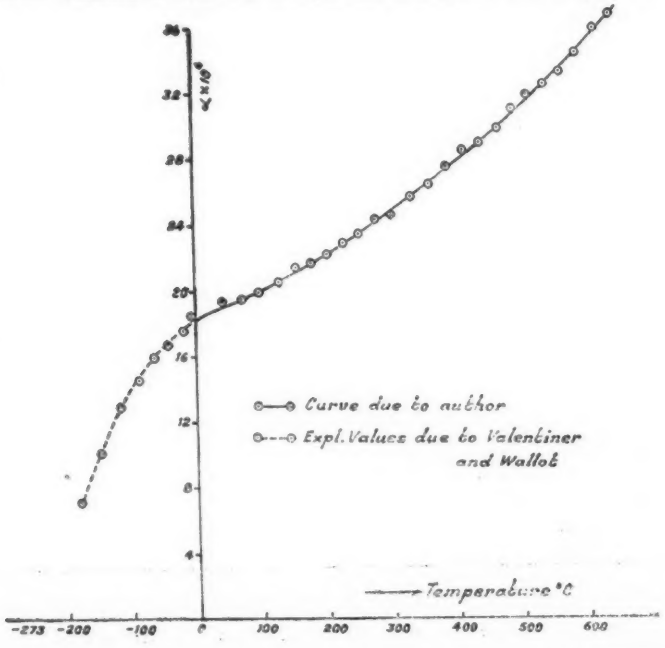

FIG. 4. Variation of coefficient of linear expansion of fluorite with temperature.

in Fig. 1 correspond to the values obtained in the two runs of the experiment with magnetite. The variation of the coefficient of linear expansion with temperature is depicted graphically in Figs. 3 and 4 for magnetite and fluorite respectively. The dotted part of the curve in Fig. 4 is drawn with the values taken from Landolt and Bornstein tables (1923) which are based on the experimental results of Valentiner and Wallot (1915).

In Table VI are collected all the quantitative data regarding the thermal expansion of these crystals, available in the literature, and the values obtained by the author are entered in the third column for comparison. The author's values have been interpolated from the formulæ referred to above. It was not possible to compare the author's values of thermal expansion for magnetite at higher temperatures with those of the earlier workers because of the lack of numerical data concerning the earlier work as mentioned in Section 2. From a perusal of the values given for fluorite, it would be readily seen that though the values of the author and those due to Press are in fair agreement after 150°C, the values of the latter are consistently much higher than the author's values below this temperature. This may partly be due to the fact that he employed a graphical method for evaluating the coefficients of expansion.

5. Discussion

The study of the thermal expansion of magnetite reveals very interesting features. There is a continuous and progressive rise in the expansion curve up to the Curie-temperature (about 570° C) after which there is a sudden decrease, as observed by previous workers. The fall in the curve is exhibited by a hump in the expansion curve II of Fig. 1. The two branches of the curve—one below the Curie-point and the other above it—when extrapolated, have different inclinations with the temperature-axis, as shown by the dotted extensions of the curve in the diagram. Afterwards the curve does not show any discontinuity or anomalous behaviour up to the highest temperature investigated (710°C). From this it follows that the magnetic transformations do not influence the thermal dilatation after the Curie temperature in contradiction to the observation of Chaudron and Forrestier referred to in Section 2. The sharp fall in the magnitude of the thermal expansion at the Curie-point is quite conspicuous in Fig. 2 which depicts the variation of the coefficient of thermal expansion with temperature. It is significant to note that at the Curie-temperature not only the absolute value of the coefficient of thermal expansion markedly falls but its rate of variation with temperature thereafter is less than its previous value below the Curie temperature. During the run of the experiment it was found that

the interference pattern retained its configuration unaltered as the specimen crossed the Curie-point, both during heating and cooling processes, indicating thereby that the transformations in the magnetite are strictly reversible in nature.

As the present study furnishes values for the coefficient of expansion for this crystal over a sufficiently wide range of temperature, and as specific heat data are available in the literature throughout this range, Grüneisen's theory (1912, 1926) can be put to test. For specific heats, the data are available from the measurements of Weiss and Beck (1908) (290°-1065° K) Weiss, Piccard, and Carrard (1919) (artificial magnetite, 296°-954°K; natural 654°-928°K), Roth and Bertram (1929) (369°-1056° K), Esser, Averdick and Grass (1933) (473°-1273° K). The four sets of result are in fair agreement, but those of Roth and Bertram are the most consistent. According to Kelley (1934), who studied the experimental data of all these investigators, "the heat absorption at the magnetic inversion point (if any) is too small to necessitate separate consideration, and the data may be adequately represented by only one equation given below:—

$$C_p = 41{\cdot}17 + 18{\cdot}82 \times 10^{-3}T - 9{\cdot}795 \times 10^{5}T^{-2}" \qquad (1$$

The accuracy claimed by Kelley for this equation is 2% and the temperature interval for its validity is from 270° K to 1065° K. For the present paper, the values of C_p for magnetite at different temperatures have been calculated by making use of equation (1) and are entered in the second column of Table VI. The molar specific heat at constant volume, C_v, has been calculated by making use of the well known relation—

$$C_p - C_v = AC_p^2T \text{ where } A = 0{\cdot}994 \times 10^{-6}.$$

The values of C_v so calculated are entered in the third column of the same table. The values of the coefficients of expansion, α, entered in the fourth column, are calculated by making use of the appropriate formula given at the top of Table III.

The compressibility, χ, of magnetite has been measured by Madelung and Fuchs (1921), Bridgman (1925) and Adams (1927). The values of all these investigators are in fair agreement. For the present calculations, the value of compressibility as given by Bridgman at 30° C and under normal atmospheric pressure has been employed. Similarly for V_0, the molecular volume of magnetite at absolute zero of temperature and under no external pressure, the value used is 44·69 c.c. which is the value under normal conditions of temperature and pressure.

The values of γ, the Grüneisen's constant, are entered in the last column of Table VII. From a perusal of these values it is at once apparent that

the variation of γ with temperature is extremely marked. Up to 160° C. its value remains sensibly constant, but thereafter it continuously increases up to the Curie temperature at which there is an abnormal fall in its value,

TABLE VII. *Grüneisen's constant for magnetite at different temperatures*

$V_0 = 44{\cdot}69$ c.c. $\qquad$ $\chi_0 = 0{\cdot}541 \times 10^{-12}$ cm.²/dyne.

Temperature (° C.)	C_p Cals. deg.$^{-1}$ mole.$^{-1}$	C_v Cals. deg.$^{-1}$ mole.$^{-1}$	$\alpha \times 10^6$ deg.$^{-1}$	$\gamma = \frac{3\alpha V_0}{\chi_0 C_v}$
50	37·86	37·40	8·72	1·38
100	41·15	40·52	9·24	1·35
150	43·66	42·86	9·96	1·37
200	45·70	44·72	10·89	1·44
250	47·43	46·26	12·02	1·53
300	48·97	47·60	13·36	1·66
350	50·38	48·81	14·91	1·80
400	51·68	49·89	16·67	1·97
450	52·91	50·90	18·64	2·16
500	54·08	51·83	20·80	2·37
550	55·21	52·72	23·19	2·60
580	55·87	53·23	21·94	2·43
620	56·84	53·96	23·93	2·62
660	57·50	54·53	26·04	2·82
700	58·45	55·14	28·28	3·03

but subsequently its value again increases slowly. The variation of γ with temperature is represented graphically in Fig. 5. The abrupt change in

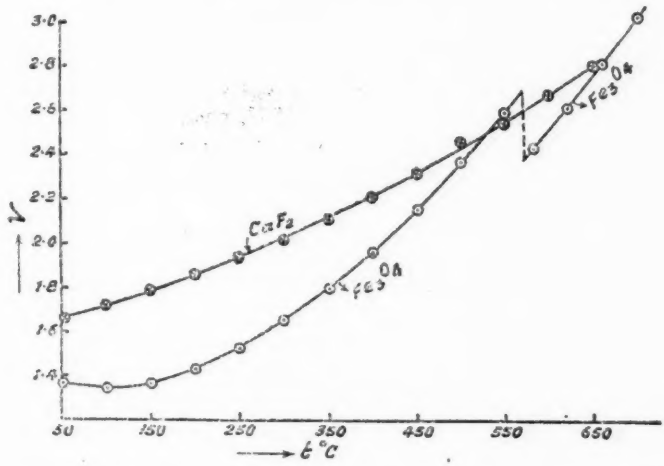

FIG. 5. Variation of Grüneisen's constant for Fe_3O_4 and CaF_2 with temperature.

the value of γ above the Curie-temperature in magnetite indicates some kind of atomic rearrangement in the crystal, and is probably accompanied by a change in the lattice constant. X-ray studies of magnetite at these temperatures may throw more light on these conclusions.

It was with the fluorite crystal that Grüneisen himself (1918) could satisfactorily explain the existing data on thermal expansion by Valentiner and Wallot (1915) by assuming a constant value for $\gamma = 1{\cdot}7$. Press (1949) from his measurements on thermal expansion above the room temperature showed that γ exhibits a definite temperature dependence. Let us examine how far Grüneisen's law is valid at higher temperatures. Krestovnikov and Karetnikov (1934) were the first to make heat content measurements up to about 1273° K. Later Lyashenko (1935) reported measurements upto 1590° K. The recent accurate measurements are those of Naylor (1945) who has studied the heat absorption not only in the condensed phase, but beyond the melting point (1691° K) for the liquid phase also. According to him the experimental data on the heat absorption can be represented by the following equation:—

$$H_T - H_{298{\cdot}1} = 14{\cdot}30\,T + 3{\cdot}64 \times 10^{-3}\,T^2 - 0{\cdot}469 \times 10^5\,T^{-1} - 4430 \quad (2)$$

This equation is applicable for the temperature region from 298° K to 1424° K and the accuracy claimed by its author is 0·3%. The molar specific heat at constant pressure is thus given by

$$C_p = \left(\frac{\delta H}{\delta T}\right)_p = 14{\cdot}30 + 7{\cdot}28 \times 10^{-3}\,T + 0{\cdot}469 \times 10^5\,T^{-2} \quad (3)$$

The values of C_p calculated with the aid of equation (3) are entered in the second column of Table VIII and the corresponding temperatures are listed in the first column. The values of C_v entered in the third column of this table are calculated by making use of the relation

$$C_p - C_v = 5{\cdot}32 \times 10^{-6} \cdot C_p^2 \cdot T.$$

The values of α, entered in the fourth column, are interpolated by making use of the formula given at the top of Table V. The compressibility for fluorite has been measured by Madelung and Fuchs (1921) and Bridgman (1925). According to the latter the compressibility at 30° C. is given by the formula—

$$\chi_{30} = 1{\cdot}206 - 6{\cdot}69 \times 10^{-6} p \ (\mathrm{cm^2 kgm^{-1}}) \quad (4)$$

From this relation the value of χ_{30} under zero external pressure comes out to be $1{\cdot}23 \times 10^{-12}$ cm.²/dyne. This value has been employed for evaluating the Grüniesen's constant, the values of which are entered in the last column

of Table VIII. The variation of γ with temperature is represented graphically in Fig. 5. From a perusal of these values it is evident that γ, instead of remaining constant, varies from 1·66 at 50° C. to 2·81 at 650° C.

TABLE VIII. *Grüneisen's constant for fluorite at different temperatures*

$V_0 = 24{\cdot}56$ c.c. $\qquad \chi_0 = 1{\cdot}23 \times 10^{-12}$ cm²/dyne.

Temperature (° C.)	C_p Cals. deg.$^{-1}$ mole.$^{-1}$	C_v Cals. deg.$^{-1}$ mole.$^{-1}$	$\alpha \times 10^6$ deg.$^{-1}$	$\gamma = \frac{3\alpha V_0}{\chi_0 C_v}$
50	17·10	16·60	19·30	1·66
100	17·35	16·76	20·21	1·72
150	17·64	16·94	21·22	1·79
200	17·95	17·14	22·33	1·86
250	18·28	17·35	23·56	1·94
300	18·62	17·56	24·89	2·02
350	18·96	17·76	26·33	2·11
400	19·30	17·97	27·88	2·21
450	19·65	18·17	29·53	2·32
500	20·01	18·36	31·65	2·46
550	20·36	18·55	33·17	2·55
600	20·72	18·72	35·15	2·68
650	21·07	18·90	37·23	2·81

In conclusion, the author expresses his deep sense of gratitude to Prof. R. S. Krishnan for his valuable discussions during the course of these investigations.

The author's thanks are also due to Prof. Sir C. V. Raman for the loan of the fluorite crystal from his crystallographic collection and to Dr. C. S. Pichamuthu, Director, Department of Geology and Survey, Government of Mysore, for kindly putting some two dozens of magnetite crystals at the disposal of the author.

6. SUMMARY

With the help of interferometric method, thermal expansion of magnetite (upto 710° C) and fluorite (upto 650° C.) has been studied. In the case of the former the coefficient of expansion has been found to vary from $8{\cdot}70 \times 10^{-6}$ at 41·3° C. to $24{\cdot}20 \times 10^{-6}$ at about 570° C. (the Curie-point), after which there is a sudden fall in its value. It is found that thereafter the magnetic transformations have no perceptible effect on the thermal expansion. For fluorite the coefficient of expansion has been found to vary from $19{\cdot}36 \times 10^{-6}$ at 43° C. to $36{\cdot}70 \times 10^{-6}$ at 637·3° C. Grüneisen's constant has been calculated for both these crystals and is found to vary considerably with temperature.

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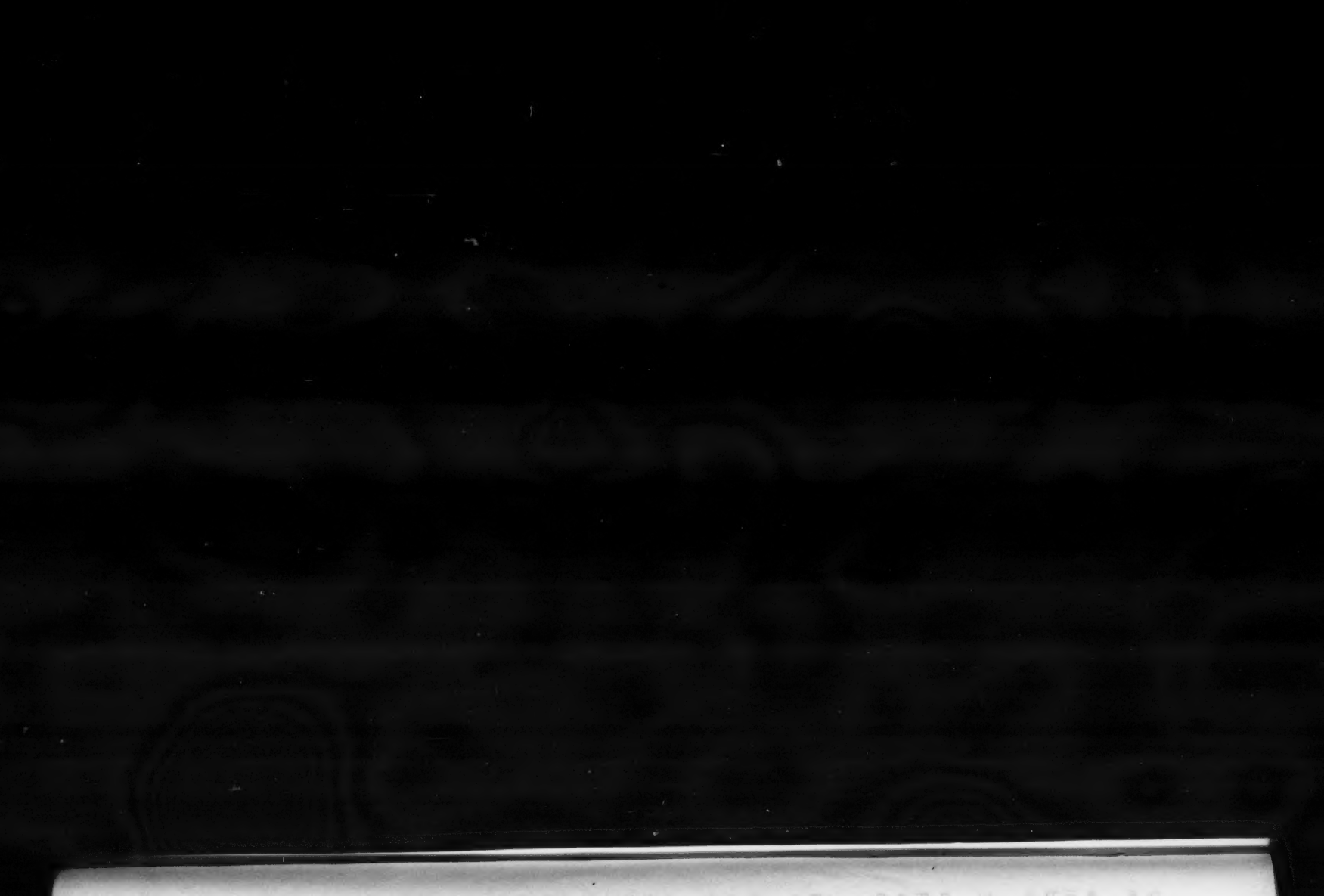
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